

# GEOCHEMISTRY

A Translation of

ГЕОХИМИЯ

o. 4

1959

## CONTENTS

avlenko, A. S., E. E. Vainshtein, and N. V. Turanskaya. Certain regularities in the behavior of rare earths and yttrium in magmatic and postmagmatic processes . . . . .	357
osterin, A. V. The possible modes of transport of the rare earths by hydrothermal solutions . . . . .	381
olodov, N. A. Certain regularities of distribution of rare elements in sharply zoned granite pegmatites . . . . .	388
adalov, S. T., and M. P. Enikeev. Geochemistry of cadmium in the Almalyk and Altyn-Topkan mineralized areas of the Karamazar region . . . . .	406
yanov, V. V., and N. V. Lizunov. Indium in some tin deposits of Yakutia . . . . .	416
idinyan, R. Kh. Distribution of rare alkalis in soil colloids and the participation of plants in this process . . . . .	428
bramovich, I. I. Uranium and thorium in the intrusive rocks of Central and Western Tuva . . . . .	442
leksandrov, I. V. On the peculiarities of evolution of the rocks of the Krivoi Rog series resulting from alkali metasomatism . . . . .	451
akhrushev, V. A. Mineralogical-geochemical zoning in the iron deposits of the Kondoma region of Gornaya Shoriya . . . . .	471

*Published by*  
**The Geochemical Society**

# GEOCHEMISTRY

A translation of the journal of the Academy of Sciences, U. S. S. R.,  
devoted to geochemistry

A publication of the Geochemical  
Society, supported financially by  
a grant from the National Science  
Foundation.

Officers of the Society, 1960

T. F. W. Barth, President  
Mineralogisk Museum  
Oslo 45, Norway

Harold C. Urey, Vice-President  
University of California  
La Jolla, California

Konrad B. Krauskopf, Secretary  
Department of Geology  
Stanford University, California

George T. Faust, Treasurer  
U. S. Geological Survey  
Washington 25, D. C.

John F. Schairer, Past President  
Geophysical Laboratory  
Washington 8, D. C.

## Councilors

E. F. Osborn, 1958-1960  
Pennsylvania State University  
University Park, Pennsylvania

H. G. Thode, 1958-1960  
McMaster University  
Hamilton, Ontario

Albert E. J. Engle, 1959-1961  
California Institute of Technology  
Pasadena 4, California

Friedrich G. Houtermans, 1959-1961  
Physikalisches Inst. Univ. Bern  
Sidlerstrasse 5, Berne, Switzerland

Thure G. Sahama, 1960-1962  
University of Helsinki  
Helsinki, Finland

Ralph S. Cannon, 1960-1962  
U. S. Geological Survey  
Federal Center, Bldg. 25  
Denver 14, Colorado

Translation Editor... E. Ingerson  
Managing Editor... J. Winchester

Editorial Assistant: Margaret N. Everett  
Board of Associate Editors: Leason H.  
Adams, F. R. Boyd, Paul E. Damon, Mi-  
chael Fleischer, Jack Green, E. P. Hend-  
erson, T. S. Lovering, Duncan McCon-  
nell, Donald McGannon, Jack Vallyntyne,  
D. E. White.

## Subscription Prices

Per year (eight issues). . . . . \$20.00

To members of the Geochemical  
Society and to educational  
institutions . . . . . \$10.00

Single copies . . . . . \$2.00 and \$4.00

Subscriptions and orders should be ad-  
dressed to the Geochemical Society and  
sent to

Prof. Earl Ingerson  
Dept. of Geology  
The University of Texas  
Austin 12, Texas

## TRANSLITERATION

There is no ideal system of translit-  
erating Russian; each has its advantages  
and disadvantages. For the translation of  
Geokhimiya we have chosen the system  
used by Chemical Abstracts, partly be-  
cause of its wide acceptance by other  
journals and partly because of certain  
advantages in alphabetization of names.  
The principal differences between this  
system and others in common use are as  
follows:

Russian	Chem. Abs.	Others
X	kh	h
ц	ts	tz
ш	shch	sch
ю	yu	iu
я	ya	ia

Translated by

ROYER and ROGER, Inc.



## CERTAIN REGULARITIES IN THE BEHAVIOR OF RARE EARTHS YTTRIUM IN MAGMATIC AND POSTMAGMATIC PROCESSES

A. S. PAVLENKO, E. E. VAINSHTEIN  
and N. V. TURANSKAYA  
V. I. Vernadskii Institute of Geochemistry  
and Analytical Chemistry  
Academy of Sciences USSR, Moscow

It was shown in several earlier papers [1-9] that the ratios of the elements with similar chemical properties forming geochemical pairs and groups (Nb-Ta, Zr-Hf, rare earths--Y) are strongly dependent on the character of the geological processes causing their migration and concentration. The factors having dominant effect on the ratios of pairs and groups of elements are most conveniently studied within a single area containing rocks sufficiently different in age, petrographic character and origin so that the effect of regional variation in clarkes is excluded. In the present research the rare earth minerals from the localities in Eastern Tuva were used. The data on the Zr/Hf and Nb/Ta ratios in the minerals of Eastern Tuva and the basic geological information on the structure of the region and of the individual massifs in it were published earlier [5, 7]. Here only the main points needed for the discussion will be noted. The igneous rocks to which the rare earth mineralization is related are divisible into two large complexes, the Middle Paleozoic,  $\gamma\text{Pz}_2$  Syutkhol' granites and the later alkalic  $\epsilon\text{Pz}_2$  complex. The alkalic complex is divided into two phases. The first is represented by different nepheline syenites, mainly of the miaskitic type but including syenites and quartz syenites -  $\epsilon\text{Pz}_2$ , and the second, by syenites and alkalic granites -  $\epsilon\text{Pz}_2$ . The Syutkhol' and the alkalic complexes belong to separate successive tectonic-magmatic stages of the Middle Paleozoic time. The rocks of the first and the second phases of the alkalic complex are comagmatic but are separated by an episode of tectonic movements, mainly of the dislocation type. The fact that the two phases are comagmatic is proved by the unity of petrochemical evolution, areal connections and the common structural pattern of emplacement.

In order to discuss the characteristics of the rare earth mineralization and the ratios among the members of this group of rare metals, it is logical to separate the following rock types: orthomagmatic rocks, pegmatites, autometasomatic rocks and endocontact metasomatites including the high

Table 1

Distribution of Rare Earth Minerals in the Rocks of Eastern Tuva

Genetic type		Syutkhol' complex. Granites	Alkalic complex		
			1st phase	2nd phase	
			Nepheline syenites	Syenites and alkalic granites	
Igneous rocks		Monazite (23)	Pyrochlore (1)	Chevkinite*	Pyrochlore (2, 3) --chevkinite (13, 14)
		Allanite (29, 30)	Chevkinite (12)	Allanite	Euxenite (46--51) --monazite (24--25)
			Eudialyte Rinkolite		Euxenite (52) Xenotime
Pegmatites		Fergusonite (34--38)	Pyrochlore (4)	Fergusonite (40) --	Pyrochlore (5, 6) --chevkinite (15, 16)
		Fergusonite (39) -- cheralite (28)	Eschynite (47)	gadolinite (46)	Euxenite (53) -- monazite (26)
			Eudialyte Rinkolite		Chevkinite (18) -- fergusonite Fergusonite (41) -- allanite (31) Britholite (20)
Metasomatic rocks	Auto-metasomatic		Pyrochlore	Fergusonite (42--45)	Pyrochlore (8, 9) --chevkinite (18)
			Chevkinite	Parisite (33)	Pyrochlore (7) -- monazite (27) Euxenite (54--60) Thorite (61)**
	Exocontact		Pyrochlore (10) Britholite (21) Rinkolite		Pyrochlore (11) Britholite (22) Allanite (32)

Numbers after mineral names are analysis numbers as given in tables 2, 3 and 4. Absence of a number indicates that the mineral was not analyzed.

\* Although powder photographs of the mineral give typical chevkinite pattern, x-ray - chemical analysis did not detect rare earths.

\*\* Thorite contains 5.33% of rare earths. X-ray- chemical analysis was made on the separated rare earth oxides.



temperature hydrothermal veins.

Only those rare earth minerals were studied whose lanthanide and yttrium content could be determined directly by x-ray spectrographic analysis. These minerals were pyrochlore, fergusonite, euxenite, eschynite, parisite, monazite, a mineral of the cheralite type [5], britholite, chevkinite, allanite and gadolinite. The minerals with low rare earth content requiring preliminary chemical enrichment, such as zircon, malacon, cleveite, thorianite, fluorite, columbite and others, are not considered in the present paper. The only exception to this is thorite. The minerals of apatitic rocks are rare in the investigated region and were not studied (rinkolite, eudyalite, etc.)

The age and genetic classification of the rocks and the distribution of rare earth minerals and mineral assemblages among them are presented in Table 1. It will be seen that the available material makes it possible to determine the effect of the following factors on the ratios between individual rare earth elements in the minerals [1, 2, 3, 8, 9]:

a) a crystallochemical characteristics of the minerals, b) variation in the composition of the rare earth group with time, c) alkalinity of the rocks (in the petrographical sense), and d) the origin of the minerals. Complete solution of these problems is difficult because of the absence of rare earth minerals from some age and genetic groups of rocks and the presence of different mineral species in them. It must be mentioned that the effect of the composition of the rare earths in the enclosing sedimentary and metamorphic rocks on their ratios

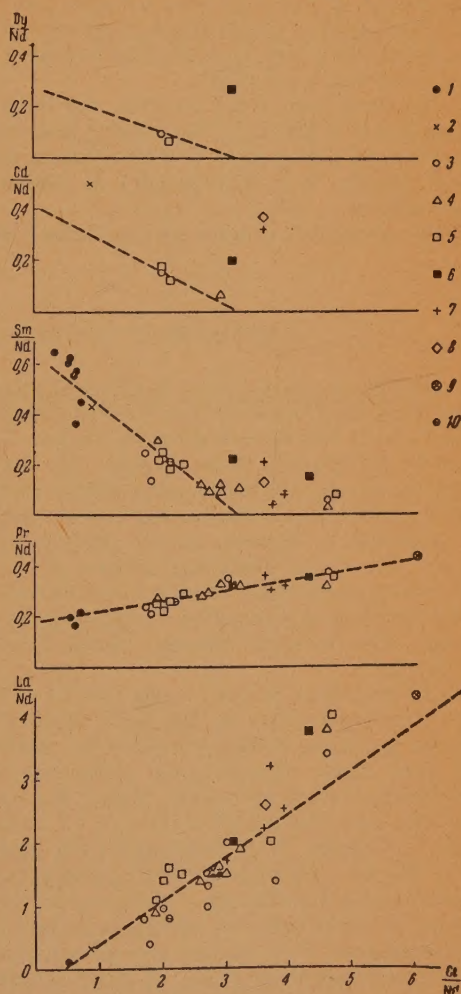


Fig. 1. The  $La/Nd$ ,  $Pr/Nd$ ,  $Sm/Nd$ ,  $Gd/Nd$  and  $Dy/Nd$  ratios as functions of the  $Ce/Nd$  ratio in selectively cerian and complex minerals

1 - fergusonite, 2 - eschynite, 3 - pyrochlore, 4 - chevkinite, 5 - monazite, 6 - britholite, 7 - allanite, 8 - gadolinite, 9 - parisite, 10 - cheralite

earths in the enclosing sedimentary and metamorphic rocks on their ratios

in the orthomagmatic and postmagmatic rocks is practically nil, first, because of the considerable uniformity of the enclosing rocks as to age and lithology and, second, because of the negligible amount of assimilation. The available material does not give information on the effect of temperature and depth of the various processes since all investigated mineral assemblages are high temperature products related to intrusions at shallow and intermediate depths.

The main part of the material for the present work was collected by the Tuva group of the V. I. Vernadskii Institute of Geochemistry and Analytical Chemistry, and a number of specimens were presented by Yu. V. Makhin, N. E. Kostin, V. I. Kudrin and I. A. Nechaev, to whom the authors tend sincere thanks.

The analytical scheme was published earlier [1].

## DISCUSSION OF EXPERIMENTAL RESULTS

Distribution of the rare earths and yttrium in the minerals. The results of x-ray-spectrographic analysis of different minerals for their rare earth and yttrium content are given in Tables 2, 3 and 4. All analyzed minerals may be divided into three groups: the dominantly cerian (chevkinite, monazite, cheralite, parisite), dominantly yttrian (euxenite) and complex minerals (britholite, allanite, gadolinite, eschynite).

Unlike E. I. Semenov [8, 9], we refer fergusonites to the complex minerals, because of their high content of cerium and neodymium. Moreover, the strong predominance of cerium earths in pyrochlores, britholites and allanites makes it possible to group them with the dominantly cerian minerals. For the same reason, thorite is placed with the dominantly yttrian minerals.

On the graphs of Fig. 1, the  $\text{La/Nd}$ ,  $\text{Pr/Nd}$ ,  $\text{Sm/Nd}$ ,  $\text{Gd/Nd}$  and  $\text{Dy/Nd}$  ratios are plotted as the functions of the  $\text{Ce/Nd}$  ratio for the dominantly cerian and some complex minerals. Attention is immediately attracted by the quite clear, almost linear dependence between these ratios in all investigated cerium minerals, which was previously established for monazites and allanites (interrupted lines) [1]. In the complex minerals, britholite (20)\*, allanite (32), gadolinite (46), eschynite (47) and some fergusonites (35, 38, 41, 45), linear relationship persists to samarium but is sharply disturbed for gadolinium. This regularity indicates that the ratios of individual cerium earths in cerium minerals are constant and do not depend on the conditions of migration and crystallochemical characteristics of the different mineral species. In this connection it will be enough to discuss one of the ratios ( $\text{Ce/Nd}$ , for example), for it determines all the rest.

The variations in the  $\text{Ce/Nd}$  ratio in the different mineral species (Table 2) lie within the following limits: in pyrochlore, 1.7 -- 4.6; in chevkinite, 1.9 -- 4.6; in monazite, 1.95 -- 4.7; in allanite, 3.0 -- 3.9; and in britholite, 3.1 -- 4.3; i.e., the ranges of variation are very similar and overlap each other. A very high value of 6 is found only in parisite (33).

When pyrochlore and chevkinite (2 and 13, 3 and 14, 5, 6 and 15, 16)

---

\* Here and below, figures in parentheses after mineral names are the sequence numbers of Tables 2, 3 and 4.



### Table 2

## Content of the Rare Earths and Yttrium in Cerium Minerals

[illegible]

Table 2 (Continued)

Name of massif	Age	Genetic type of rock	Petrographic characteristics
Orugtin	$\epsilon Pz_2^1$	Orthomagmatic	Microclinized nepheline biotite
Dugdin	$\epsilon Pz_2^2$	"	Aegirine-riebeckite granosyenite
"	$\epsilon Pz_2^2$	"	Slightly albitized quartz syenite with alkalic amphiboles
Terekhol	$\epsilon Pz_2^1$	Pegmatite	Albitized and silicified syenite of the riebeckite-aegirine quartz karaadyrite type in the border of alkalic pegmatite
Dugdin	$\epsilon Pz_2^2$	"	Riebeckite-quartz dike rock with microcline perthite relicts
"	$\epsilon Pz_2^2$	"	Same
"	$\epsilon Pz_2^2$	Autometasomatic	Albitized pegmatoidal schliere in granosyenites
"	$\epsilon Pz_2^2$	"	Pegmatoidal schliere in alkalic granitoids. Albitized and silicified aegirine granosyenite
"	$\epsilon Pz_2^2$	"	Albitized quartz-rich alkalic aegirine granite
"	$\epsilon Pz_2^1$	Contact metasomatic	Alkali amphibole albite mariupolite with microcline relicts
"	$\epsilon Pz_2^2$	"	Aegirine albitite
Terekhol	$\epsilon Pz_2^1$	Orthomagmatic	Strongly albitized biotite aegirine nepheline syenite





Table 2 (Continued)

Name of massif	Age	Genetic type of rock	Petrographic characteristics
Dugdin	$\epsilon Pz_2^2$	Orthomagmatic	Aegirine riebeckite granosyenite
"	$\epsilon Pz_2^2$	"	Slightly albitized alkali amphibole quartz syenite
"	$\epsilon Pz_2^2$	Pegmatite	Riebeckite quartz rock with microcline perthite relicts
"	$\epsilon Pz_2^2$	"	Same
"	$\epsilon Pz_2^2$	"	Same
"	$\epsilon Pz_2^2$	"	Pegmatite vein with fergusonite
"	$\epsilon Pz_2^2$	Autometasomatic	Pegmatite schlieren in alkalic granitoids. Albitized and silicified aegirine granosyenite
"	$\epsilon Pz_2^2$	Pegmatite	Pegmatite vein
"	$\epsilon Pz_2^1$	Contact metasomatic	Coarse-grained aegirine albitite
"	$\epsilon Pz_2^2$	"	Fluorite vein in idocrase skarn at granosyenite contact
Milzei	$\gamma Pz_2^1$	Orthomagmatic	Biotite granite
"	$\epsilon Pz_2^2$	"	Alaskite
Ilekteg	$\epsilon Pz_2^2$	"	Medium-grained biotite granite
Uzuntaiga	$\epsilon Pz_2^2$	Pegmatite	Brecciated and silicified granosyenite porphyry dike
Dugdin	$\epsilon Pz_2^2$	Contact metasomatic	Albitized pegmatoidal schlieren in granosyenites



Table 2 (Continued)

Content of the Rare Earths and Yttrium in Cerium Minerals

Number	No. of sam- ple	Mineral	Relative content of the rare earths and yttrium												
			La/Nd	Ce/Nd	Pr/Nd	Sm/Nd	Gd/Nd	Tb/Nd	Dy/Nd	Ho/Nd	Er/Nd	Tu/Nd	Yb/Nd	Lu/Nd	Y/Nd
28	DYa	Chera-	0.8	2.1	0.26	0.21	--	--	--	--	--	--	--	--	--
	70/5	lite													
29	1020	Allanite	2.5	3.9	0.32	0.08	--	--	--	--	--	--	--	--	--
30	E62	"	3.2	3.7	0.3	0.04	--	--	--	--	--	--	--	--	--
31	296	"	1.65	3.0	--	--	--	--	--	--	--	--	--	--	--
32	DG143	"	2.2	3.6	0.36	0.21	0.32	--	0.38	--	0.15	--	0.14	--	2.25
33	BK5/2	Pari- site	4.3	6.0	0.48	--	--	--	--	--	--	--	--	--	--

are found together, the value of Ce/Nd is lower in the former than in the latter. The opposite is true of the pair (8 and 19). When pyrochlore and monazite occur together (7 and 27), the latter has the higher Ce/Nd ratio. This is in accordance with Semenov's [8] hypothesis of the dependence of "diadochic capacity" of minerals relative to the rare earths on the coordination number of the latter, since the coordination number of the rare earths in pyrochlore is 8 and in monazites, 10.

The compositions of the rare earths and yttrium in the yttrium minerals, euxenite and thorite, recalculated to 100%, are given in Fig. 2. The general character of distribution of the rare earths is alike in all specimens and is characterized by one sharp dysprosium maximum. The peculiarity of the euxenites is the considerable variability in the content of yttrium, erbium and dysprosium and a very slight variation in the content of ytterbium, gadolinium and samarium.

It was shown by N. V. Turanskaya [3] that the ratios of the individual rare earth elements and ytterbium to erbium in xenotimes are quite constant: Ho/Er = 0.31; Dy/Er = 1.25, Tb/Er = 0.18, Gd/Er = 0.58, Sm/Er = 0.2 and Y/Er = 11.5. An examination of Table 4 shows that in euxenites these ratios have average levels corresponding to the above figures. However, there is a considerable scatter of ratio values and it cannot be concluded, as in the case of the cerium minerals, that these ratios are of general validity. As for the Y/Er ratio, its value varies within very broad limits (3.5 to 12.5) and does not exhibit a simple relation to the rare earth content. Especially sharp deviations occur in metasomatic euxenites (54-60). It is interesting that there is an antipathetic relation between the content of yttrium and the rare earths, especially of erbium and dysprosium

Table 2 (Continued)

Name of massif	Age	Genetic type of rock	Petrographic characteristics
Bayankol Ilektyag	$\gamma\text{Pz}_2$ $\gamma\text{Pz}_2$	Pegmatite Orthomagmatic	Amazonite pegmatite Leucocratic porphyritic biotite granite
Erzin	$\gamma\text{Pz}_2$	"	Biotite granite
Dugdin	$\epsilon\text{Pz}_2^2$	Pegmatite	Strongly silicified feldspar magnetite quartz dike rock
"	$\epsilon\text{Pz}_2^2$	Contact metasomatic	Orthoclase albitite
Burek- Kundus	$\epsilon\text{Pz}_2^1$	Autometasomatic	Albitized leucocratic syenite

(Fig. 2). In the igneous and pegmatitic euxenites (48-53) the content of yttrium is higher than in the metasomatic euxenites (54-60), but the reverse is true for erbium and dysprosium content.

Fig. 3 presents the content of the rare earths and yttrium in complex minerals recalculated to 100%. The assemblages of the rare earths are similar in all minerals and dysprosium and neodymium have distinct maxima. Moreover, gadolinite (45), fergusonite (40), allanite (32) and britholite (20) show a sharp cerium maximum and the yttrium content diminishes accordingly. The range of variation in the content of individual rare earths in fergusonites, eschynite and gadolinite is very similar; in allanite and britholite there is a noticeable deficiency in yttrium and the heavy rare earths, beginning with gadolinium, reflecting the cerium specialization of these minerals.

As in the case of euxenites, the distribution of yttrium content in fergusonites is antipathetic to that of the rare earths. For example, fergusonite (34) has the highest yttrium content and fergusonite (40) the lowest, but the cerium content is lower in the former than in the latter. This reversal of the order of content from yttrium to cerium becomes especially clear beginning with dysprosium and is well shown by fergusonites from individual areas, for example, from the Khusingol'skii (34-38) and Agashskii (42-45) massifs. This indicates that the relationship between the rare earths and yttrium is determined not only by the crystallochemical characteristics of a given mineral species but, as will be shown later, depends also on the conditions of its formation. Indeed, if these ratios were determined by the crystallochemical properties of a mineral, a parallel increase in the content of yttrium and yttrium earths could be expected. In reality the entire



Table 3

## Content of the Rare Earths and Yttrium in Complex Minerals

Number	No. of sample	Mineral	Relative content of the rare earths and yttrium												
			La/Nd	Ce/Nd	Pr/Nd	Sm/Nd	Gd/Nd	Tb/Nd	Dy/Nd	Ho/Nd	Er/Nd	Tu/Nd	Yb/Nd	Lu/Nd	Y/Nd
34	T109	Fergusonite	--	--	--	0.8	1.2	0.27	1.5	0.35	0.9	--	0.9	--	16.5
35	T102	"	0.3	--	--	0.65	0.75	0.23	1.0	--	0.65	--	0.8	--	10.0
36	T103	"	0.6	--	--	0.8	1.65	0.20	1.05	0.20	0.60	0.05	0.55	0.1	10.0
37	T108	"	--	0.55	--	0.75	0.95	--	0.94	0.19	0.65	--	0.59	--	7.2
38	T101	"	--	0.6	--	0.55	0.7	0.13	1.0	0.3	0.6	0.08	0.72	0.16	7.2
39	BYa671	"	--	0.23	--	0.80	0.90	0.28	1.55	0.23	0.9	--	1.1	0.19	14.0
40	D10	"	--	2.2	--	0.36	0.6	--	1.0	0.3	1.0	--	1.1	--	5.0
41	296	"	--	0.61	0.17	0.37	0.61	0.10	1.78	0.11	0.56	--	0.44	0.07	6.7
42	AG46	"	--	0.70	0.22	0.45	1.0	0.29	1.75	0.25	1.6	0.18	1.4	0.32	14.5
43	AG42	"	--	0.53	--	0.60	0.67	0.17	1.0	0.17	0.67	0.1	0.67	0.13	7.3
44	AG154	"	0.1	0.55	0.20	0.63	0.67	--	0.93	0.16	0.55	--	0.85	0.1	6.0
45	AG152	"	--	0.65	--	0.58	0.68	0.15	0.78	0.17	0.52	--	0.32	0.04	3.8
46	D42	Gadolinite	2.6	3.6	--	0.13	0.37	--	1.0	--	0.67	--	0.8	0.17	6.3
47	8/1	Eschynite	0.3	0.85	--	0.43	0.5	--	0.59	--	0.31	--	0.32	--	5.0

Table 3 (Continued)

Name of massif	Age	Genetic type of rock	Petrographic characteristics
Khusungol	$\gamma Pz_2$	Pegmatite	Border zone of spodumene pegmatite
"	$\gamma Pz_2$	"	Spodumene pegmatite
"	$\gamma Pz_2$	"	"
"	$\gamma Pz_2$	"	"
Bayankol	$\gamma Pz_2$	"	Amazonite pegmatite
Dugdin	$\gamma Pz_2$	"	Pegmatite vein
"	$\epsilon Pz_2^1$	"	Feldspar magnetite quartz dike rock. Strongly silicified
Agash	$\epsilon Pz_2^2$	Autometasomatic	Microclinized and albitized syenite with biotite, riebeckite, aegirine, fluorite and carbonate. Border metasomatic zone in the endocontact of the intrusive
"	$\epsilon Pz_2^1$	"	Microclinized and albitized biotite syenite. Slightly silicified
"	$\epsilon Pz_2^1$	"	Same
"	$\epsilon Pz_2^1$	"	Strongly microclinized biotite plagioclase microcline canelite
Dugdin	$\epsilon Pz_2^1$	Pegmatite	Pegmatite vein
Balyktyghem	$\epsilon Pz_2^1$	"	Albitized microcline nepheline mariupolite with cancrinite and fluorite



Table 4

Content of the Rare Earths and Yttrium in Dominantly Yttrium Minerals

Number	No. of sam- ple	Mineral	Relative content of the rare earths and yttrium												
			La/Er	Ce/Er	Pr/Er	Nd/Er	Sm/Er	Gd/Er	Tb/Er	Dy/Er	Ho/Er	Tu/Er	Yb/Er	Lu/Er	Y/Er
48	2530	Euxenite	-	-	-	0.26	0.26	0.45	--	1.05	--	0.14	0.14	0.32	12.5
49	3000	"	-	-	-	0.21	0.23	0.6	0.17	1.2	0.19	0.12	1.05	0.23	11.0
50	1149	"	-	-	-	--	0.60	0.9	--	1.4	--	--	1.0	--	9.0
51	1070	"	-	-	-	--	--	1.1	--	1.5	--	--	0.95	--	7.5
52	286/1	"	-	-	-	--	0.06	0.42	0.15	1.3	0.35	--	0.58	0.11	6.2
53	2653	"	-	-	-	--	--	0.9	--	1.6	--	--	1.2	--	14.0
54	100 /19	"	-	-	-	--	--	0.5	--	1.5	--	--	0.8	--	5.5
55	664	"	-	-	-	0.21	0.21	0.48	0.20	1.5	--	--	0.72	0.04	5.4
56	103 /35	"	-	-	-	--	0.19	0.54	0.22	1.45	0.3	--	0.80	0.08	5.6
57	103/4	"	-	-	-	0.05	--	0.48	--	1.35	0.3	--	0.85	0.16	4.8
58	106 /11	"	-	-	-	--	--	0.53	0.18	1.45	0.3	--	0.6	0.09	4.0
59	550	"	-	-	-	--	--	0.48	--	1.45	0.3	--	0.62	--	3.5
60	103/3	"	-	-	-	0.3	0.23	0.45	0.16	1.25	0.27	0.07	0.75	0.12	4.0
61	UT52 /2	Thorite	-	-	-	0.13	0.13	0.4	0.17	1.3	0.3	--	0.7	0.08	7.2

group of the rare earths (for example 34-39) shows an antipathetic relation to yttrium, especially dysprosium, gadolinium and samarium, whose ionic

Table 4 (Continued)

Name of massif	Age	Genetic type of rock	Petrographic characteristics
Milzei	$\epsilon Pz_2^2$	Orthomagmatic	Leucocratic alkalic biotite granite
Uzuntaiga	$\epsilon Pz_2^2$	"	Silicified calc-alkaline syenite of the larvikite-monzonite type
Milzei	$\epsilon Pz_2^2$	"	Alaskite
Ilekteg	$\epsilon Pz_2^2$	"	Medium-grained biotite granite
Dugdin	$\epsilon Pz_2^2$	"	Brecciated leucocratic amphibole biotite granite with fluorite
Uzuntaiga	$\epsilon Pz_2^2$	Pegmatite	Brecciated and silicified grano-syenite porphyry dike
Aksug	$\epsilon Pz_2^2$	Autometasomatic	Riebeckite albite cyrtolite vein
"	$\epsilon Pz_2^2$	"	" " " "
"	$\epsilon Pz_2^2$	"	" " " "
"	$\epsilon Pz_2^2$	"	Riebeckite albite schlier in albitized quartz syenite. Border zone
"	$\epsilon Pz_2^2$	"	Metasomatic riebeckite albite vein
"	$\epsilon Pz_2^2$	"	Albitized quartz syenite
"	$\epsilon Pz_2^2$	"	Riebeckite albite schliere in albitized quartz syenite. Central zone
Erzin	$\epsilon Pz_2^2$	"	Albitized and hydromuscovitized leucocratic alkalic granite porphyry

radil are nearest to that of yttrium. Unfortunately, similar observations cannot be made for other mineral species because of insufficient data.



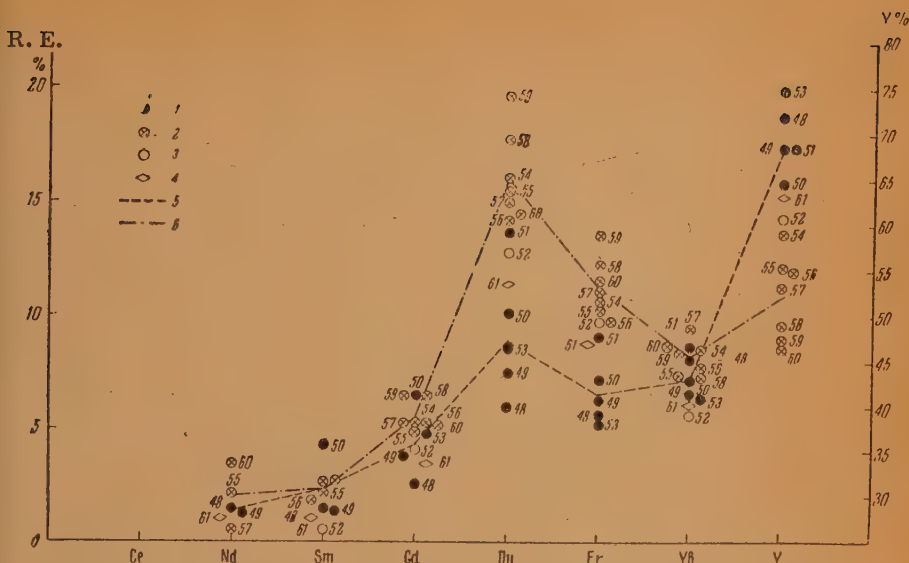


Fig. 2. Content of R. E. and Y in the dominantly yttrium minerals

1 -- accessory euxenites of igneous rocks and pegmatites, 2 -- euxenites of metasomatic rocks, 3 -- euxenites of other origin, 4 -- thorite, 5 -- curve of average content of R. E. and Y in accessory euxenites of igneous rocks and pegmatites, 6 -- curve of average content of R. E. and Y in euxenites of metasomatic rocks

Unlike the dominantly cerian and dominantly yttrian minerals, the complex minerals do not exhibit simple relations between the ratios of the individual rare earths (to Nd or Er). The La/Nd, Ce/Nd, Pr/Nd and Sm/Nd ratios form an exception to this in some fergusonites (35, 38, 41, 45, 42), eschynite (47), gadolinite (46) allanite (32) and britholite (20) and exhibit the linear relationship characteristic of cerium minerals (Fig. 1). In all other cases these ratios in the complex minerals are greater than in cerium minerals and the ratios of the heavier elements do not show any regular interdependence. This is due, first of all, to the considerable diadochic capacity of the complex minerals, which enables them to capture individual elements selectively and thus disturb the ratios usually established among the rare earth elements during the process of migration. Of interest from this point of view are fergusonite (40) and gadolinite (46), both with very high cerium content.

A comparison of the diagrams of Figs. 2 and 3 shows that there is a considerable resemblance in the distribution of the rare earths in all investigated dominantly yttrian and complex minerals. In both cases there is a sharp dysprosium maximum. This assemblage of the yttrium earths may be regarded, therefore, as typical of the investigated region and is not determined by the crystallochemical characteristics of individual minerals.

An examination of the distribution of the rare earths in individual

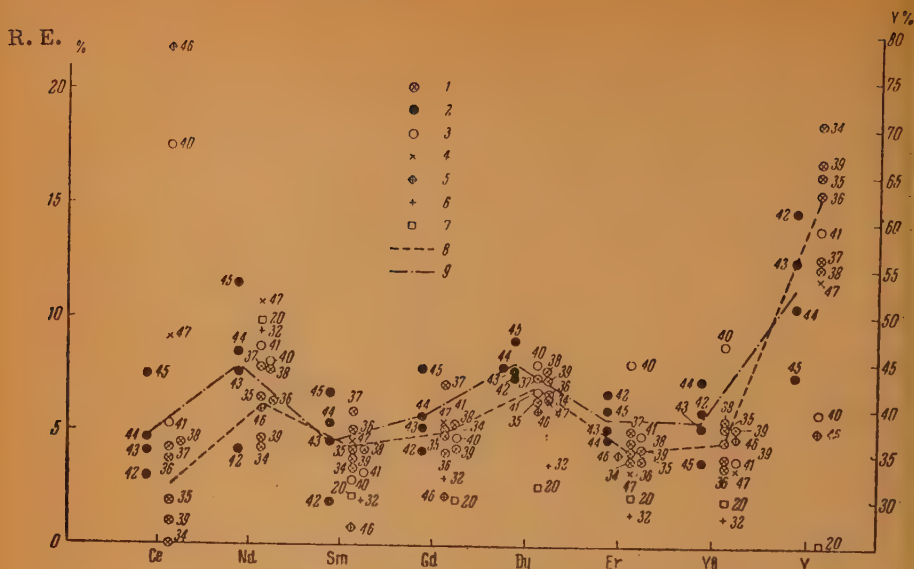


Fig. 3. Content of R. E. and Y in complex minerals

1 -- fergusonite of granite pegmatites, 2 -- fergusonites of metasomatic rocks, 3 -- fergusonites of different origin, 4 -- eschynite, 5 -- gadolinite, 6 -- allanite, 7 -- britholite, 8 -- curve of average content of R. E. and Y in fergusonites of granite pegmatites, 9 -- curve of average content of R. E. and Y in metasomatic rocks (Ce content in samples 20 and 32 and Y content in sample 32 omitted)

minerals shows that it does not depend entirely on the crystallochemical characteristics of individual mineral species but is determined for the light lanthanides (La-Sm) by the universally linear dependence between their relative content and for the heavy lanthanides (Gd-La) by the character of the assemblage characteristic for a given region. The crystallochemical characteristics of minerals determine the segment of the rare earth group which may enter into a given mineral. In individual cases, minerals with high "diadochic capacity" (complex minerals) may be selectively enriched in samarium, less frequently in the lighter elements, and thus distort the linear relationships of the cerium earths. The variations in the content of the individual rare earths in each mineral species depends on its age and the conditions of its formation.

Dependence of the composition of the rare earth assemblage in minerals on the age of the rocks. The distribution of mineral species in the rocks of different ages (Table 1) shows that yttrium minerals predominate in the rocks of the last magmatic phase, the second phase of the alkalic complex. While in the Sytkhol' granites and syenites of the first phase only the dominant cerium minerals and complex minerals with cerium specialization (monazite, chevkinite, pyrochlore, allanite) are developed, in the rocks of the second phase, dominantly yttrium minerals appear, euxenite and thorite. In the pegmatites and metasomatic rocks of the Sytkhol' granite-syenite



complex of the first phase, yttrium occurs only in the complex minerals (fergusonite, eschynite, gadolinite), while in the similar rocks of the second phase, euxenite is widespread. It should be mentioned also that in the second phase yttrium and yttrium earths appear in the complex minerals with cerium specialization such as britholite (22), allanite (35) and even thorite (61). In the older rocks these minerals are completely free of yttrium earths, for example allanite (29, 30) and britholite (21). The final differentiates of the first phase of the alkalic complex and the rocks of the second phase are quartz syenites often identical petrographically. But the rocks of the first phase contain dominantly cerian minerals and complex minerals with high cerium content, fergusonite (40, 42-45) and gadolinite (40), while the rocks of the second phase contain dominantly yttrium minerals. This suggests that the impoverishment of the rocks of the second phase in cerium earths cannot be explained wholly by the degree of alkalinity of the rocks but is related to the general evolution of the magmatic chamber in time.

A comparison of the composition of the rare earths in the cerium minerals of different ages shows a shift towards yttrium in the younger rocks. The Ce/Nd ratio in the pyrochlores of the first phase of the alkalic complex (1, 4, 10) is higher than in the pyrochlores of similar rocks of the second phase (2, 3, 5, 6, 11). The same is true of chevkinites (12-13, 14), britholites (21-22) and the monazites of the Syutkhol' granites (23) and granosyenites of the second phase (24, 25).

It was noted earlier that the complex minerals of the younger rocks are enriched in yttrium earths while the allanites of the ancient granites (29, 30) have relatively high Ce/Nd ratios ranging from 3.9 to 3.7. The variation in the composition of the rare earths in fergusonites does not show a definite dependence on the age of the rocks, due, probably, to the leveling effect of the pegmatitic process and the high "diadochic capacity" of fergusonites. A somewhat higher cerium content in a fergusonite (41) from a pegmatite of the second phase may be due to the later intensive silicification.

These facts show convincingly enough that yttrium and yttrium earths are accumulated in the minerals of the final stage of magmatic evolution.

The effect of alkalinity of the rocks on the composition of the rare earths is revealed by comparing the nepheline syenites of the first phase with granitic rocks. All minerals associated with nepheline syenites have a high content of the cerium earths. Characteristically, the nepheline syenite pegmatites carry eschynite rich in the cerium earths instead of fergusonite and euxenite. The minerals of nepheline syenites, pyrochlore (1, 4, 10), chevkinite (12) and britholite (21) have high Ce/Nd ratios.

A very high cerium content in fergusonite (40), gadolinite (46), and parisite (33) must be explained, apparently, by an intimate genetic relationship between nepheline syenites and the syenites of the first phase.

Thus in Eastern Tuva the higher concentration of the cerium earths in the rocks of the first phase as compared with the older and younger rocks must be explained by the strong alkalinity, and this is in agreement with Fersman's idea that the cerium earths are enriched in alkalic rocks in preference to the yttrium earths.

The dependence of the composition of the rare earths on the genetic type of rocks is manifested by the character of distribution of the mineral species. The yttrium-bearing complex minerals (fergusonite, eschynite, gadolinite and britholite (20)) occur mainly in pegmatites. The ortho-magmatic and metasomatic rocks are characterized by cerium minerals. The yttrium minerals are absent from the exocontact metasomatites, even

from those related to the second phase of the alkalic complex enriched in yttrium earths.

In the cerium minerals the Ce/Nd ratio shows a definite dependence on the genetic type of rocks in which the minerals occur. In general the ratio is lower in the pegmatites than in the orthomagmatic phases and higher in the metasomatites, as has already been noted for monazites [1, 3]. The following minerals may be mentioned as examples: monazite (23), cheralite (28), pyrochlores (2-5, 6-7, 8, 9, 11), chevkinites (13, 14-15, 17, 18), monazites (24, 25-27), allanites (31-32), britholites (20-22). It has been mentioned repeatedly [2, 4] that this is undoubtedly the result of difference in the mobility of the individual rare earths during magmatic and postmagmatic evolution. The increase in solubility and stability of the complex compounds from the cerium to the yttrium earths must insure accumulation of the heavier elements in the closed pegmatitic systems and the preferential removal of these elements from the metasomatic zones.

Similar regularities are observed in fergusonites and euxenites. The specimens with the highest yttrium content among the Khusuingol'skii and Agashskii fergusonites (34 and 42) came from the first marginal pegmatite belonging to the second endocontact facies bordering on metasomatized marbles and far removed from the main group of pegmatites. In these cases there is a characteristic complete correlation between the behavior of Hf and the rare earths on the one hand and of Zr and Y on the other, the Zr/Hf ratio in zircons 34 and 42 being about twice as high as in zircons with lower yttrium content (Table 3). It should be noted that fergusonites occur only in the cupolas of the Agashskii massif near xenoliths and roof pendants. This indicates that the marginal parts of the massif are enriched in the yttrium earths. On the other hand, the fergusonite (45) with the lowest yttrium content and the highest cerium among the Agashskii fergusonites occurs in a metasomatic rock of the canadite type containing abundant microcline, while other fergusonite-bearing rocks (42-44) are intensively albitized. It is natural that potash metasomatism should result in the most complete removal of the yttrium earths since the solubility curve of the lanthanide-carbonate complexes has a steeper curve when potassium is present instead of sodium [10].

In the diagram of Fig. 4 the compositions of the euxenites are clearly enough divided into two groups, the accessory euxenites of orthomagmatic rocks and pegmatites and the euxenites of autometasomatic rocks. A specimen from a dike of leucocratic granite porphyry (58) has the highest yttrium content, while a specimen of the same mineral from autometasomatic rocks (54-60) has the lowest yttrium content and the highest content of erbium, dysprosium and the cerium earths. Among the Aksugskii euxenites the highest yttrium content is found in the specimens from metasomatic veins (54, 56). The yttrium content in the euxenites 60 and 57 is revealing. The first comes from the central part of a metasomatic schlieren zone, the second, from the marginal zone. Being related to more intensive metasomatism, euxenite 60 has a lower yttrium content.

The fergusonites from the autometasomatic rocks of the Agashskii massif (42-45) form a quite definite group with a lower yttrium and higher lanthanide content as compared with the specimens from granitic pegmatites (34-39). However, it is hard to say whether this is a result of "metasomatic shift" or of the general enrichment of the first phase of the alkalic complex in the cerium earths. Fig. 4 shows the compositions of fergusonites recalculated to 100% after the subtraction of the amounts of lanthanum, cerium, praseodymium, neodymium, samarium, gadolinium and dysprosium



corresponding to the linear relationship of these elements to Nd in the cerium earths (Fig. 1). The compositions of the fergusonites are shown, therefore, minus the natural background of the cerium earths, and the persistent lower yttrium content in fergusonites 42 and 45 must evidently be regarded as a result of "metasomatic shift."

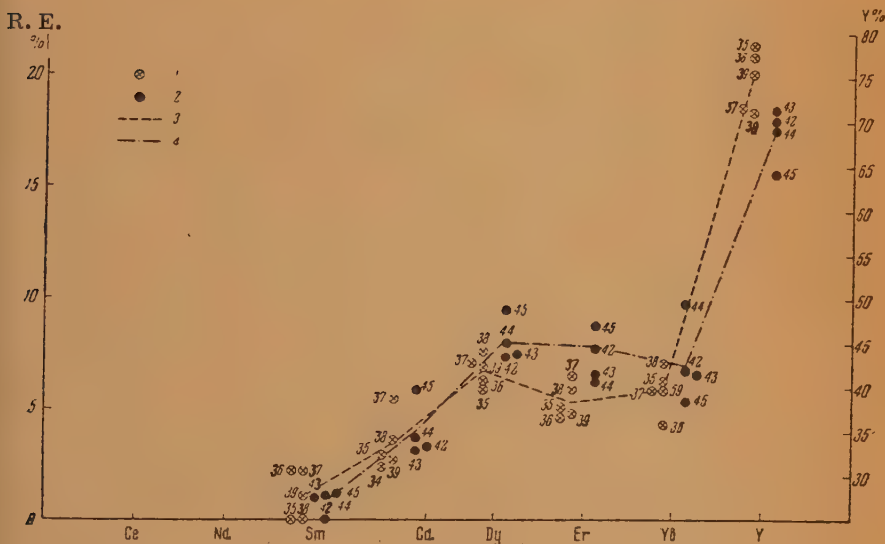


Fig. 4. Content of yttrium earths and yttrium in fergusonites of granite pegmatites and metasomatic rocks

1 -- fergusonites of granite pegmatites, 2 -- fergusonites of metasomatic rocks, 3 -- curve of average content of rare earths and yttrium in fergusonites of granite pegmatites, 4 -- curve of average content of rare earths and yttrium in metasomatic rocks

An examination of the diagrams of Figs. 3 and 4 reveals differences in the behavior of yttrium and the yttrium earths. In the Agashskii fergusonites (42-45) the yttrium content is lower than in the fergusonites from granitic pegmatites (34-39), but the total rare earth content is higher. This is especially clearly shown by the content of ytterbium, erbium, dysprosium, neodymium and cerium. The content of samarium and gadolinium is very similar in both groups. The diagram of Fig. 2 shows that the accessory euxenites from orthomagmatic rocks (48-51, 53) are richer in yttrium and poorer in the rare earths than the euxenites of the Ak-sug but have very nearly the same samarium and gadolinium content. The similarity in the character of change in the composition of the rare earths in fergusonites and euxenites due to metasomatism is shown still more clearly by a graph of relative increment in the average content of individual rare earth elements in the minerals of the metasomatic rocks as compared

with orthomagmatic rocks and pegmatites (Fig. 5). By relative increment ( $\Delta$ ) we mean the ratio of the difference in the average content of a given element in minerals from rocks of different origin to the average content of the element in a given mineral species. The amount of the increment must reflect the mobility of the element during metasomatism and is evidently inversely proportional to it; i. e., the more the element is accumulated in

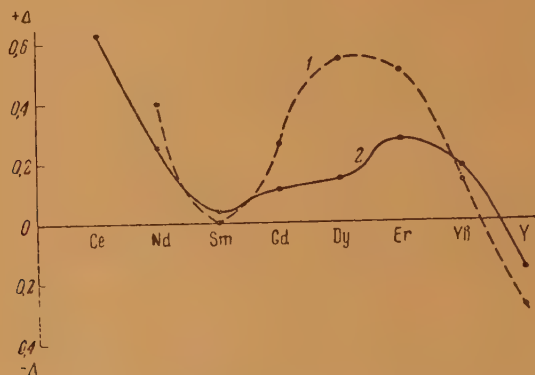


Fig. 5. Relative increase in the average content of R. E. and yttrium in fergusonites and euxenites of metasomatic rocks as compared with igneous rocks and pegmatites

1 -- curve of relative increase in the content of R. E. and Y in euxenites, 2 -- curve of relative increase in the content of R. E. and Y in fergusonites

the solid phase (mineral) the lower its mobility in the metasomatizing solution. The character of distribution of the increments (or mobilities) on the curves of Fig. 5 cannot be explained simply by the changes in the chemical properties of the lanthanides-yttrium group, for they are usually represented by smooth curves. In particular, the solubility and stability of the complex compounds which determine the mobility of the lanthanides in solutions decrease uniformly from lanthanum to lutecium. Evidently the curves of Fig. 5 are determined by at least two factors, the chemical properties of the elements (mainly the property of forming complexes) and the crystallochemical characteristics of the minerals. The first factor depending on the increase in mobility from the cerium to the yttrium earths is reflected in the downward trending segments of the curves (Ce-Sm, Er-Y) and in the general tendency towards a shift in the direction of the lanthanides in the metasomatic minerals. The effect of the crystallochemical characteristics of the minerals is reflected in the greater increments in the yttrium earths with a maximum for erbium due to the selective capturing of these elements by the fergusonite and euxenite lattices. The importance of the crystallochemical

factors is confirmed also by the position of samarium (Fig. 5), which can be explained by the equal effect of these factors on Sm and Y, two elements with identical ionic radii (0.97Å).

The high content of the cerium earths in the minerals of the exocontact metasomatites, pyrochlore (10, 11), britholite (21, 22) and allanite (32) has already been mentioned. At the same time, it is precisely in the metasomatized zones of the enclosing rocks that the precipitation of the yttrium earths brought in by the postmagmatic solutions could be expected. That this does not occur must evidently be due to the considerable stability of the yttrium complexes in the highly alkaline metasomatizing solutions and to the essentially carbonate composition of the enclosing rocks in the investigated region. These two factors favor dispersion of yttrium and the yttrium earths and inhibit the formation of independent yttrium earth minerals. It should be noted, however, that in metasomatic zones far removed from igneous contacts the yttrium earths may appear in such complex minerals as allanite (32).

Thus, an examination of the data on the effect of genetic factors on the character of distribution of the rare earths and yttrium in the minerals of genetically different rocks shows that as compared with the orthomagmatic rocks the pegmatites accumulate yttrium and the yttrium earths and the metasomatic rocks are impoverished in them. Both in pegmatites and in metasomatites a relative enrichment in yttrium and the yttrium earths occurs in the areas far removed from the centers of infiltration of metasomatizing solutions or in the pegmatites of the cupolas. In the autometasomatic rocks the accumulation of cerium earths is determined by the intensity of metasomatism, a relatively more complete removal of the yttrium earths occurring in the case of potash rather than soda metasomatism. In the autometasomatic processes, yttrium exhibits a much greater mobility than the rare earths, and as a result the minerals of autometasomatites are relatively enriched in the lanthanides as compared with postmagmatic and pegmatitic minerals. The changes in the composition of the rare earths during metasomatism are determined not only by the chemical properties of the lanthanides, which change gradually, but also by the crystallochemical characteristics of the minerals.

A comparison of the behavior of the rare earths and yttrium with that of the pairs Zr-Hf and Nb-Ta under various geological conditions shows that the ratios within the lanthanide-yttrium group are more complex and are governed by a larger number of factors. It was shown in references [4, 5] that the Zr/Hf ratio in zircons depends mainly on the alkalinity and the genetic type of the rocks, while the Nb-Ta ratio is determined by the age of mineralization [7]. Moreover, the rare earth assemblage in minerals depends on the ratios between individual rare earths which may be universal (in the cerium subgroup) or merely characteristic of a certain region (in the yttrium subgroup) rather than a given mineral species and its crystallochemical characteristics.

The variation in the ratios within the rare earths-yttrium group and in the niobium-tantalum ratios with time shows that there is a complete analogy between the behavior of the yttrium earths and yttrium and that of niobium, since all these elements become concentrated in the latest magmatic complexes.

An increase in the alkalinity of the rocks leads to the concentration of zirconium and the cerium earths, due, apparently, to the higher solubility of the alkalic complexes of  $\Sigma Y^*$ , and hafnium. The analogy between  $\Sigma Y$

\* $\Sigma Y$  stands for the yttrium earths (Dy-Lu) and Y.



Table 5

Minerals	Geological characteristics	Relative content of Y	Zr/Hf*
Fergusonites (35-39) Fergusonite (34)	Pegmatites Apex of a pegmatite	Y/Nd 7.2 - 14.0 16.5	6.5 - 6.9 12
Fergusonites (43-45) Fergusonite	Albitized and micro- clinized syenites Metasomatized apex of a syenite intrusion	3.8 - 7.3  14.5	29 - 31  70
Euxenite (60)	Central part of metasomatized schlieren	Y/Er 4.0	2.9
Euxenite (57)	Border of a metasomatized schlieren	4.8	42
Euxenite (56)	Metasomatic vein	5.6	145
Pyrochlore (3) Pyrochlore (9)	Quartz syenite Albitite developed after quartz syenite	Ce/Nd 1.8  2.7	68  44

\* These figures were obtained on zircon associated with the rare earth minerals. The analyses were made in the spectrographic laboratory of the Institute of Geochemistry and Analytical Chemistry. I. D. Shevaleevskii, analyst.

and hafnium is shown also by the fact that these elements accumulate together in pegmatites. The behavior of  $\Sigma Y$  and Hf in infiltration autometasomatism, however, is directly opposite, and, as can be seen from Table 5, the yttrium earths behave like zirconium. The autometasomatized rocks become relatively enriched in the cerium earths and hafnium, while  $\Sigma Y$  and Zr become concentrated on the margins of the metasomatic zones far away from the center of infiltration. It must be understood, of course, that the magnitude of change in the content of the individual lanthanides is not a direct function of their chemical properties, but depends also on the crystallochemical characteristics of the minerals (Fig. 5). According to our data, the exocontact metasomatites also concentrate cerium earths and zirconium. This, however, is not due to a change in the ability of yttrium and the yttrium earths to migrate but to the greater stability of their soluble compounds and the resulting dispersion of these elements.

This comparison of the behavior of zirconium-hafnium and the rare

earths-yttrium shows that the chemical properties of the latter, mainly the solubility and stability of their complexes, play the dominant role in their migration and concentration at all stages of mineral formation. The zirconium-hafnium ratios during the process of magmatic differentiation and formation of pegmatites are also determined by the chemical properties of the elements. But in infiltration metasomatism, difference in atomic weights begins to play a role and hafnium becomes less mobile. In the rare earths-yttrium group this is manifested by the general lag of the rare earths behind yttrium during metasomatism.

### Summary

1. The assemblage of the rare earths and yttrium in the minerals concentrators is determined mainly by the proportion of the individual elements during the process of mineral formation and by their ability to migrate, and does not, on the whole, depend on the crystallochemical characteristics of the mineral species.

2. The existence of a simple linear relationship among the ratios of the light lanthanides (La-Sm) in the cerium minerals and in some complex minerals, previously established for monazites and allanites, has been confirmed and indicates that the character of these ratios is general.

The constancy of the ratios of the heavy lanthanides and yttrium--Ho/Er, Dy/Er, Tb/Er, Gd/Er, Sm/Er and Y/Er--previously established for xenotimes, is exhibited in part by euxenites but not by the complex minerals, in which these ratios do not show any simple regularities. The similarity of the heavy rare earths (Gd-Lu) and yttrium assemblages with a maximum for Dy in all complex and dominantly yttrium minerals is, evidently, a regional characteristic.

3. Variations in the absolute and relative content of the lanthanides and yttrium, as shown by the general relations among these elements, depend basically on the age of the rocks, their alkalinity and the genesis of the minerals.

4. The crystallochemical characteristics of minerals determine which part of the lanthanide-yttrium group may enter into a given mineral. For instance, when several cerium minerals occur together, that mineral has the highest Ce/Nd ratio in which the rare earths have the highest coordination number. Sometimes the crystallochemical factors distort the universal lanthanide ratios in minerals (for example, the linear relationship of the ratios among the cerium earths in fergusonites) or the ratios determined by the chemical properties of the elements, by their ability to migrate (high yttrium earth content in the metasomatic fergusonites and euxenites).

5. The final products of magmatic evolution within a region become enriched in yttrium and the yttrium earths.

6. The highly alkalic igneous complexes containing nepheline syenites are enriched in the cerium earths whatever the relative age of the rocks.

7. The genetic features of the processes of mineral formation have the following effects on the ratios in the lanthanide-yttrium group: a) a relative concentration of yttrium and the yttrium earths occurs in pegmatites and the marginal parts of metasomatic zones; b) the shift towards the cerium earths increases with the intensity of metasomatism, and the rare earths as a group exhibit less mobility than yttrium; c) a more thorough removal of the rare earths is caused by potash than by soda metasomatism.

8. All the relationships among the rare earths and yttrium arising in the course of migration in space and time and in different geochemical environments point to the relatively higher mobility of the yttrium earths and yttrium as compared with the cerium earths. This is best explained by the increasing solubility and stability of the complex lanthanide compounds (for example, the alkali carbonate complexes) towards the yttrium earths.

The lesser mobility of the rare earths as compared with yttrium during infiltration metasomatism may be due to the difference between the atomic weights of the rare earths and yttrium. This insures the greater mobility of yttrium.

9. A comparison of the behavior of Zr-Hf, Nb-Ta and RE-Y under similar conditions shows that the relationships among the rare earths and yttrium are more complex and depend on a larger number of factors. This is explained, first of all, by the fact that, chemically, yttrium is an analogue of the yttrium earths (Dy-Er-Yb), crystallochemically, it is an analogue of samarium, and yet it is more mobile than the lightest of the lanthanides. Therefore, during the general magmatic evolution the EY group, like niobium and zirconium, is concentrated in the latest magmatic complexes. In the processes causing change in the alkalinity of the rocks and in pegmatites the EY group behaves like hafnium and is concentrated or removed together with it. In the metasomatic processes the rare earths behave like hafnium and tantalum, but yttrium behaves like zirconium and niobium.

#### REFERENCES

1. Vainshtein, E. E., A. I. Tugarinov and N. V. Turanskaya (1956). *Geokhimiya*, No. 2.
2. Tugarinov, A. I. and E. E. Vainshtein (1958). V sb. Doklady Simposiuma po Geokhimii Redkikh Elementov v Svyazi s Problemoi Petrogenezisa (in the collection: Reports of the symposium on the geochemistry of rare elements in connection with the problem of petrogenesis). Izd. Akad. Nauk SSSR.
3. Turanskaya, N. V. (1958) *Razrabotka Metodov Rentgeno-Spektral'nogo Analiza Redko - Zemel'nykh Elementov i ikh Primenenie dlya Geokhimii* (Methods of x-ray - spectrographic analysis and their application to geochemistry). Dissertation, Moscow.
4. Tugarinov, A. I., E. E. Vainshtein and I. D. Shevaleevskii (1956). *Geokhimiya*, No. 4.
5. Pavlenko, A. S., E. E. Vainshtein and I. D. Shevaleevskii (1957). *Geokhimiya*, No. 5.
6. Vainshtein, E. E., A. I. Tugarinov, A. M. Tuzova and I. D. Shevaleevskii (1958). *Geokhimiya*, No. 3.
7. Pavlenko, A. S., E. E. Vainshtein and M. M. Kakhana (1958). *Geokhimiya*, No. 6.
8. Semenov, E. I. (1957). *Geokhimiya*, No. 7.
9. Semenov, E. I. and R. L. Barinskii (1958). *Geokhimiya*, No. 4.
10. Sklyarenko, Yu. S. (1953). Dissertation. V. I. Vernadskii Institute of Geochemistry and Analytical Chemistry, Acad. Sci. USSR, Moscow.

Received for publication  
October 23, 1958.



## THE POSSIBLE MODES OF TRANSPORT OF THE RARE EARTHS BY HYDROTHERMAL SOLUTIONS

A. V. KOSTERIN

V. I. Vernadskii Institute of Geochemistry  
and Analytical Chemistry,  
Academy of Sciences USSR, Moscow

Apart from the monazite placers, large economic concentrations of the rare earths are found in hydrothermal deposits [1, 2, etc]. For this reason the question of the form in which the rare earths were transported by hydrothermal solutions from the magmatic chamber is of considerable interest.

It is necessary, first of all, to clarify the nature of these hydrothermal solutions.

The majority of the rare earth deposits are related to alkalic rocks and occur as veins and irregular metasomatic bodies in metamorphic and igneous rocks. The rare earth mineralization is most commonly represented by bastnaesite, parisite and monazite, usually associated with Ca, Fe and Mg carbonates, less frequently with potash-soda feldspars, quartz, hydrous iron oxides, fluorite and thorium silicates. Often small amounts of zircon, sulfides (pyrite, galena), aegirine, biotite and other minerals are present. In some deposits there are large accumulations of barite. Thus, the minerals of the rare earth deposits are characterized by the presence of the cations K and Na, which form strong bases, and of the anions of weak and intermediate acids such as  $\text{H}_2\text{CO}_3$  and HF.

The cation and anion composition of the minerals in the rare earth deposits, the presence of minerals which can form only from alkaline solutions (Ca, Fe, Mg carbonates, parisite, etc.) and the definite genetic relation of the deposits to alkalic rocks indicate that the hydrothermal solutions responsible for the rare earth mineralization were alkaline. The alkaline nature of the solutions is confirmed also by the fact that such an alkalic mineral as aegirine often crystallizes from them. The mineralogy of the rare earth deposits shows that the ore solutions contained large amounts of anions of carbonic ( $\text{HCO}_3^-$ ,  $\text{CO}_3^{2-}$ ) and hydrofluoric acids ( $\text{F}^-$ ) and, in some cases, of sulfuric acid ( $\text{HSO}_4^-$ ,  $\text{SO}_4^{2-}$ ).

The rare earths could not have been transported in these solutions as simple ions, for they would have been immediately precipitated either as hydroxides or as carbonates, fluocarbonates and fluorides. Therefore, in

order to be carried for any distance, the rare earths had to exist in the solutions in the form of easily soluble, difficultly dissociated compounds or complexes.

Inasmuch as the rare earths do not form any stable soluble compounds with  $\text{HCO}_3^-$  and  $\text{HSO}_4^-$  [3], the possibility must be considered that they were transported in the form of complexes with  $\text{CO}_3^{2-}$ ,  $\text{F}^-$  and  $\text{SO}_4^{2-}$  anions strongly concentrated in the solutions.

1. The  $\text{CO}_3^{2-}$  anion. Experimental studies show that the rare earths form easily soluble stable complexes with this anion [4]. It is known, for instance, that when an alkali carbonate is added to the solution of a rare earth element the latter is precipitated as a carbonate. The precipitate, however, dissolves on the addition of an excess of the alkali carbonate and the greater the excess the larger the amount of the rare earth element passing into solution. According to Yu. S. Sklyarenko [4], the solution of the initial precipitate is due to the formation by the rare earth cations of an easily soluble complex of the  $[\text{RE}(\text{CO}_3)_3]^{3-}$ . Up to 0.12 g/l La and up to 6.63 g/l Y may pass into solution in this form.

The complex of the  $[\text{RE}(\text{CO}_3)_3]^{3-}$  type may evidently form in the natural high temperature alkaline carbonate solutions. This is proved by direct geological observations.

a) In the shonkinite, mafic monzonite and syenite of the Bearpaw mountains, W. T. Pecora and J. H. Ber [5] found calcite veins with sanidine, biotite, aegirine, pyrite and sometimes with barite containing rare earth carbonates; burbankite, calkinitite, ancylite and lanthanite. The rare earth minerals crystallized in the following sequence: 1) burbankite ( $\Sigma(\text{RE})_2\text{O}_3 \sim 10\%$ ), 2) ancylite ( $\Sigma(\text{RE})_2\text{O}_3 \sim 49\%$ ), (usually secondary after burbankite) and 3) calkinitite and lanthanite, (often formed at the expense of ancylite) ( $\Sigma(\text{RE})_2\text{O}_3 \sim 55-62\%$ ).

Thus, the content of the rare earths increases in the successively crystallized rare earth minerals. In the opinion of the authors this is due to the action of carbonate hydrothermal solutions carrying considerable amounts of the rare earths on the earlier minerals.

b) Still clearer is the example described by W. Jaffe and R. Meyrowitz from Mountain Pass, California [6]. Here, foliated metamorphics and alkaline igneous rocks (shonkinite, syenite, quartz syenite) contain veins and irregular bodies of barite-dolomite rock containing small amounts of galena and hematite and the rare earth minerals--sahamalite, parisite and bastnaesite--crystallized in the following sequence: 1) bastnaesite ( $\text{RE F CO}_3$ ), 2) parisite ( $2 \text{ RE F CO}_3 \cdot \text{CaCO}_3$ ) formed from bastnaesite, and 3) sahama-lite  $[(\text{Mg}, \text{Fe}) \cdot (\text{RE})_2(\text{CO}_3)_4]$ , formed later from parisite and dolomite. There is a gradual increase in the  $\text{CO}_3^{2-}$  content in the rare earth minerals and a decrease in the fluorine content. This is due, evidently, to the reaction between the bastnaesite-bearing barite-dolomite rock and the hydrothermal solutions with high rare earth and  $\text{CO}_3$  content but devoid of fluorine. If fluorine had been present in the solutions, bastnaesite and parisite would have formed instead of sahama-lite.

In solving the problem of the possible mode of transport of the rare earth elements in these localities, it should be noted, first of all, that in both cases the hydrothermal solutions were alkaline, as is indicated by the occurrence of rare earth carbonates and fluo-carbonates, which are unstable in acid solutions. Moreover, the only anion present in these solutions in notable amounts was  $\text{CO}_3^{2-}$ . Inasmuch as the rare earths cannot be transported in such solutions as free ions, the only possible form of transport in both cases could have been a complex compound containing the

only available anion --  $\text{CO}_3^{2-}$ .

Thus, both the experimental data and geological observations show that the rare earths can be carried by high temperature alkaline carbonate solutions in the form of a  $[\text{RE}(\text{CO}_3)_3]^{3-}$  complex.

2) The  $\text{F}^-$  anion. Experimental work [7, 8] shows that this anion may form easily soluble stable compounds with the rare earths. It was observed [7] that in solutions containing high concentrations of  $\text{Fe}^{3+}$ ,  $\text{Zr}^{4+}$ ,  $\text{Al}^{3+}$  and some other cations the rare earth fluorides are incompletely precipitated. This, as shown by the work of I. P. Alimarin and F. I. Pavlotskaya [8], is due to the formation of easily soluble, little dissociated complexes of the type:  $\text{RE F}_3 \cdot \text{FeF}_3$  or  $\text{RE FeF}_6$ .

The necessary condition for the formation of these complexes is a considerable excess of the cations  $\text{Fe}^{3+}$ ,  $\text{Zr}^{4+}$ ,  $\text{Al}^{3+}$  and others over the rare earths. When the ratio  $\text{Ce} : \text{Fe}^{3+} \approx 1:400$ , no complex slightly ionized compounds form, and cerium is completely precipitated by HF as a fluoride. Only when the ratio  $\text{Ce} : \text{Fe}^{3+} \approx 1:2000$  does Ce remain completely in solution.

That the rare earths are transported by hydrothermal solutions in the form of these complexes is possible, since in some rare earth-thorium deposits there is a considerable predominance of  $\text{Fe}^{3+}$  over the rare earths.

At the Old Bed mine, Mineville, New York [2], the magnetite ore bodies contain small amounts of hornblende, augite, quartz and feldspar and also fluorapatite carrying from 4.28 to 32.4% of the rare earths.

In the Gallinas Mountains, New Mexico [2], bastnaesite occurs in the fluorite deposits containing much goethite.

It is quite probable that a certain part of the rare earth content at these localities was introduced by hydrothermal solutions in the form of compounds of the  $\text{RE FeF}_6$  type.

As had already been mentioned, some of the rare earth deposits (for example, in the Wet Mountains, Colorado, and in the Blue Mountains [2, 9]) contain large amounts of sulfate in the form of barite. It is interesting to consider the possibility of transport of the rare earths in the form of a sulfate complex.

The experimental data [10, 11, etc.] show that the rare earths form easily soluble double salts with  $\text{SO}_4^{2-}$ , which in the opinion of some investigators [12] are actually complexes of the  $[\text{RE}(\text{SO}_4)_3]^{3-}$  type. When present in these compounds, the rare earths may be dissolved in large amounts in excess of  $\text{K}_2\text{SO}_4$ ,  $\text{Na}_2\text{SO}_4$  and  $(\text{NH}_4)_2\text{SO}_4$ . The saturated  $\text{K}_2\text{SO}_4$  solutions dissolve 10 g/l of  $\text{Gd}_2\text{O}_3$  (at  $35^\circ\text{C}$ ) or 49 g/l  $\text{Y}_2\text{O}_3$  at room temperature. As the temperature rises the solubility of the rare earths decreases slightly. It was shown by G. G. Urazov et al [13] that as the temperature increases from  $25$  to  $75^\circ$ , the solubility of La in an excess of  $(\text{NH}_4)_2\text{SO}_4$  decreases by a factor of five to seven. It should be expected, therefore, that in natural solutions with temperatures of  $150^\circ\text{C}$  and higher the solubility of the rare earths in the form of sulfate complexes will be somewhat lower than at room temperature, but, judging by the figures cited, it will still be sufficiently high for a part of the rare earths to be transported by the hydrothermal solutions in this form.

At the Bearpaw Mountains locality [5], cavities are occasionally found containing only barite and calkinsite, and so it is quite probable that a certain part of the rare earths had been transported in the form of a sulfate complex.

In summarizing everything that has been said about the form in which the rare earths are transported by hydrothermal solutions, the following



points should be noted:

1) It is probable that the rare earths are most frequently transported in the form of a complex of the  $[\text{RE}(\text{CO}_3)_3]^{3-}$  type, which carries the bulk of the rare earths of hydrothermal deposits.

2) At the rare earth deposits there is usually no great excess of the  $\text{Fe}^{3+}$ ,  $\text{Al}^{3+}$ ,  $\text{Zr}^{4+}$  and other cations over the rare earths such as is needed for the formation of the weakly ionized complexes of the  $\text{RE FeF}_6$  type, and it is probable, therefore, that these complexes play a very small role in the transport of the rare earths by hydrothermal solutions.

3) The transport of the rare earths in the form of sulfate complexes or double sulfate salts can be important only in deposits containing large amounts of the sulfate ion.

Inasmuch as the main mass of the rare earths in the deposits was brought in by hydrothermal solutions in the form of a complex of the  $[\text{RE}(\text{CO}_3)_3]^{3-}$  type, it is necessary to consider in greater detail the causes leading to the destruction of this complex and the crystallization of the rare earth minerals.

The  $[\text{RE}(\text{CO}_3)_3]^{3-}$  complex dissociates according to the scheme (omitting the intermediate steps)  $[\text{RE}(\text{CO}_3)_3]^{3-} = \text{RE}^{3+} + 3\text{CO}_3^{2-}$ , and since the stability constant of the complex (constant for a given temperature) is

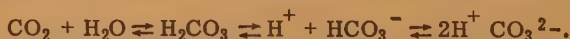
$$K = \frac{[\text{RE}(\text{CO}_3)_3]}{[\text{RE}][\text{CO}_3^{2-}]^3}$$

We have

$$[\text{RE}(\text{CO}_3)_3] \rightleftharpoons K [\text{RE}] [\text{CO}_3^{2-}]^3$$

The last equation shows that the stability of the complex depends basically on the concentration of the  $\text{CO}_3^{2-}$  ions; i. e. an increase in the concentration of these ions will stabilize the complex while a decrease in concentration will cause dissociation.

The  $\text{CO}_3^{2-}$  ions form as a result of solution of carbon dioxide in water and the subsequent dissociation of carbonic acid according to the equation:



It follows from this equation that  $[\text{CO}_3^{2-}] = \frac{[\text{CO}_2]}{[\text{H}^+]^2}$ , i. e. that the con-

centration of  $\text{CO}_3^{2-}$  in the solution is directly proportional to the amount of dissolved carbon dioxide and inversely proportional to the hydrogen ion concentration.

The decrease in the  $\text{CO}_3^{2-}$  concentration in the solution, the resulting breakdown of the  $[\text{RE}(\text{CO}_3)_3]^{3-}$  complex and the crystallization of the rare earth minerals may be caused by the following processes taking place separately or, more frequently, together.

1. Carbon dioxide may be released by decrease in pressure. The frequently observed filling of various cavities and fractures in the rocks with the rare earth minerals may be ascribed to this process.

2. The hydrogen ion concentration may increase. Most frequently this is caused by the fixation of the cations of strong bases, K, Na and others, in the wall rocks or in the rocks through which the hydrothermal solutions percolated. The near-vein alteration in the rare earth deposits suggests

this process, for it usually consists in albitization and formation of potash feldspars, hornfelses, etc.

3. The concentration of the  $\text{CO}_3^{2-}$  ion in the solution may be lowered by the fixation of the ion in some insoluble compounds. Most frequently these are various Ca, Mg and Fe carbonates often found in large accumulations in the rare earth deposits.

The rare earths are divided into the yttrium and cerium subgroups differing slightly in chemical properties. The two subgroups behave differently during the transport by hydrothermal solutions.

As was shown above, the transport of the rare earths by hydrothermal solutions is accomplished mainly in the form of the complex of the  $[\text{RE}(\text{CO}_3)_3]^{3-}$  type. The stability of this complex is different for the two subgroups: the yttrium earths form a stabler carbonate complex than the cerium earths, as can be easily seen from the table [4].

Solubility of the Yttrium and Cerium Subgroups in Excess of  $\text{K}_2\text{CO}_3$

Concentration of $\text{K}_2\text{CO}_3$	Solubility in g/l		cY/cLa ratio
	La	Y	
1 N	0.04	0.09	~ 2
2 N	0.06	0.11	~ 2
3 N	0.08	1.27	~ 16
5 N	0.12	6.63	~ 55

The yttrium earths also form a considerably more stable sulfate complex.

While the cerium earths are relatively insoluble in the saturated  $\text{K}_2\text{SO}_4$  solution [15], the yttrium earths dissolve in it in large amounts,  $\text{Y}_2\text{O}_3$ , for example, dissolves to the extent of 49 g/l [11].

The main mass of the rare earths is carried by hydrothermal solutions in the form of a carbonate complex and in some deposits, in the form of a sulfate complex. As a result of the difference in the stability of the complex for the yttrium and cerium subgroups, the ratios of these two subgroups change during the transport from the magmatic chamber to the place favorable for deposition, and the concentration of the more soluble yttrium earths increases. The relative enrichment in the yttrium earths may be accelerated by the crystallization of the minerals capturing the cerium earths from the solution (monazite, allanite, thorite and others) or slowed down by the crystallization of minerals capturing the yttrium earths (xenotime, zircon and others).

### Summary

1. The main mass of the rare earths in hydrothermal deposits was most probably brought in by solutions in the form of a  $[\text{RE}(\text{CO}_3)_3]^{3-}$  complex.

In some deposits containing large amounts of barite the rare earths could have been brought in by solutions in the form of sulfate complexes and double salts.

The transport of the rare earths in the form of fluoride complexes is evidently unimportant because of the absence in the hydrothermal solutions of the required excess of the  $\text{Fe}^{3+}$ ,  $\text{Al}^{3+}$ ,  $\text{Zr}^{4+}$  and other cations over the rare earths.

2. If the complex of the  $[\text{RE}(\text{CO}_3)_3]^{3-}$  type is the principal form in which the rare earths are transported by hydrothermal solutions, then the main causes of the breakdown of the complex and the crystallization of the rare earth minerals are:

a) Decrease in pressure resulting from the entry of the solutions into cavities and fractures.

b) Decrease in alkalinity of the solutions due to the fixation of the cations of strong bases (K and Na) by the reaction between the solutions and the country rock.

c) The fixation of  $\text{CO}_3^{2-}$  in insoluble carbonates precipitated from the solution (calcite, siderite, etc.).

3) Because the yttrium earths form much more stable carbonate and sulfate complexes than the cerium earths, the former become relatively enriched in the hydrothermal solutions. This process may be accelerated by the crystallization of minerals removing the cerium earths from the solutions, or be slowed down or even reversed by the formation of minerals preferentially withdrawing the yttrium earths.

### REFERENCES

1. Kerr, P. F. (1956) Peaceful uses of atomic energy, v. 6, 5, New York.
2. Twenhofel, W. S. and K. L. Ruck (1956). Peaceful uses of atomic energy, v. 6, 562, New York.
3. Vickery, R. C. (1953) Chemistry of the lanthanons, New York - London.
4. Sklyarenko, Yu. S. (1953) Dissertation. V.I. Vernadskii Institute of Geochemistry and Analytical Chemistry. Moscow.
5. Pecora, W. T. and J. H. Ber (1953). Amer. Mineralogist, 38, 11-12, p. 1169.
6. Jaffe, W. and R. Meyrowitz (1953). Amer. Mineralogist, 38, 9-10, p. 741.
7. Short, H. and W. Dutton (1948). Analyt. Chem., 20, p. 1073.
8. Alimarin, I. P. and F. I. Pavlotskaya (1958) O Vydelenii Redkozemel'nykh Elementov v Vide Oksalatov i Fluoridov v Prisutstvii Bol'shikh Kolichestv Drugikh Elementov (Separation of the rare earths in the form of oxalates and fluorides in the presence of a large number of other elements). In: Rare earths. Izd. Akad. Nauk SSSR, Moscow, p. 162.



9. Eingewald, Q.D. and M.R. Brock (1956). Peaceful uses of atomic energy, v. 6, 578. New York.
10. Marignac, C. (1880) *Analyt. chim. acta* (S), 20, 505.
11. Bohm, R. (1905) *Die Darstellung der Seltenen Erden*, B.I.
12. Ryabchikov, D.I. (1949) *Vvedenie k knige D. Yost, G. Russell, K. Garner, Redkozemel'nye Elementy i ikh Soedineniya* (Introduction to the book: *The Rare Earths and their Compounds* by D. Yost, H. Russell and K. Garner). *Izd. in. lit.*
13. Urazov, G.G., V.B. Tulina, V.E. Plyushchev and N.N. Chuikova (1955). *Doklady*, 103, No. 4, *Izd. Akad. Nauk SSSR*, p. 635.
14. Jaffe, H.W. (1956). *Bull. Geol. Soc. America*, 66, p. 1247.
15. Urbain, G. (1900). *Analyt. Chim. acta*, 19, 184.

Received for publication  
December 29, 1958.

## CERTAIN REGULARITIES OF DISTRIBUTION OF RARE ELEMENTS IN SHARPLY ZONED GRANITE PEGMATITES

N. A. SOLODOV

Institute of Mineralogy,  
Geochemistry and Crystal Chemistry of Rare Elements,  
Academy of Sciences USSR, Moscow

The author spent eight years in the study of internal structure and rare metal mineralization of granite pegmatites of the Altai Mountains and Kola Peninsula. These studies led to the discovery of a number of regularities in the distribution of rare elements in pegmatite bodies. Before discussing these distributions, it is necessary to describe briefly the zonal structure of the pegmatites investigated, because the distribution of rare metals is most clearly seen relative to such zoning.

All investigated pegmatites may be divided into four main types on the basis of their essential minerals: (I) microcline, (II) albite-microcline, (III) albite and (IV) albite spodumene pegmatites. Quartz is equally abundant in all of them and is therefore omitted from the type names.

It has been shown quite clearly by detailed geological mapping of numerous pegmatites that the pegmatite bodies of each type are composed of definite paragenetic groups of zones (Table 1). Although some of the zones are common to two or three types, each paragenetic group of zones is characterized by a specific composition. The microcline pegmatites are composed mainly of microcline zones, i.e., essentially quartz microcline with graphic, pegmatoid or blocky structure. The albite-microcline pegmatites contain albite, microcline and mixed albite and microcline zones. In the albite pegmatites the bulk of the vein consists of albite zones. Finally, the albite-spodumene pegmatites are composed of albite- and spodumene-bearing zones.

Brief characteristics of the zones encountered in the pegmatites investigated are given in Table 1. In addition, a pattern of spatial distribution of the zones in the pegmatitic bodies exists. First of all, in the steeply dipping pegmatites the zones of each paragenetic group always succeed each other from the border to the core in the order given in the table.

Depending on the physicochemical conditions of formation of the pegmatites, two or several adjacent zones of a given paragenetic group may be spatially undifferentiated and coalesce into a single zone. This is particularly characteristic of the zones of blocky quartz and blocky microcline, which often form a common blocky quartz-microcline phase.

Due to various causes, one or several zones of a paragenetic group may be omitted. This may happen in the border areas, especially in the apex of a vein, or in the pinching out of veins and their offshoots in central zones. The intermediate zones also may be omitted. The omission of zones is a very common occurrence, and only a few pegmatitic bodies contain all those characteristic of the given type of pegmatite. Most pegmatites are composed of only two or three zones.

Neither the coalescence nor the omission of zones disturbs their sequence from the border to the core. This is a remarkable law of the internal structure of pegmatites, and no exceptions to it have been found in the steeply dipping pegmatites of the region investigated.

The internal structure of gently dipping pegmatites is usually asymmetrical:

1) A zone developed on both borders of a vein is usually thicker on the footwall. Blocky microcline (I) and zones of coarse muscovite are the only exceptions to this rule: they are usually thicker on the hanging wall.

2) Very often the border zone developed on the footwall is completely absent from the hanging wall and its place is taken by the next zone of the paragenetic group. In some pegmatites (especially albite and albite-microcline pegmatites) several zones may be omitted on the hanging wall.

Passing to the description of the regularities of distribution of rare elements among granite pegmatite zones, it should be said at the outset that it is based on the study of only two pegmatite regions and does not claim to be universally valid. However, the author found no significant deviations from these regularities in the extensive literature on pegmatites.

Most rare metal minerals, both in quantity and number of species, occurs in the albite and albitized zones. This has already been noted in the literature [2, 8] and especially emphasized by K. A. Vlasov, who showed that pegmatites of type IV, the rare metal replacement type, are the most promising as ores of rare metals. In the albite zones such rare metal minerals occur as tantalite, columbite, microlite, simpsonite, stibiotantalite, spodumene, petalite, montebrasite, lithiophilite, beryl, pollucite, cassiterite and others, and also rubidium-rich minerals (pink muscovite, lepidolite and late generations of microcline) in amounts of practical importance.

Smaller but still economically important amounts of rare metal minerals are associated with mica zones. The muscovite zones usually contain only tantalite-columbite, beryl and cassiterite, while the lepidolite zones contain only lepidolite, tantalite and, less frequently, pollucite and cassiterite.

Finally, a very insignificant role in rare metal mineralization is played by the zones in which microcline is the essential mineral; neither the graphic or pegmatoid quartz-microcline nor the monomineralic blocky microcline zones contain economically important concentrations of rare metal minerals. Only large prismatic crystals of beryl developed in the blocky quartz-microcline zone are to some extent paragenetically related to microcline, because they are usually found on the boundaries between the microcline and quartz masses. The other rare metal minerals (tantalite-columbite, cyrtolite, uraninite, etc.) occurring in the quartz-microcline zones, with graphic, pegmatoid or blocky structure, are the products of albitization, silicification, muscovitization and other replacement processes.

The predominant localization of rare metal minerals in the mica and particularly albite zones does not mean that all albite or muscovite phases are equally promising as prospects for rare metals. Investigations of economic occurrences of rare metals show that different albite and mica zones located in different parts of a pegmatite body contain entirely different rare metal minerals (Table 1). Thus, the zone of fine-grained platy albite in all pegmatites in which it is developed contains abundant tantalite, pollucite, vorobyevite and pink spodumene, while in the zone of saccharoidal albite only columbite is found in large amounts. Similarly, the quartz-muscovite zone always carries columbite and beryl and sometimes cassiterite. The zone of scaly muscovite contains only tantalite, and the zone with large sheets of muscovite is practically devoid of rare metal minerals.



Table 1  
Zones of Rare Metal Pegmatites

Zones (the name of a zone indicates its most characteristic structure and principal minerals)	Minerals of secondary importance and typomorphic minerals	Position in the pegmatite body	Typical content of rare elements, %					
			BeO	Ta <sub>2</sub> O <sub>5</sub> + Nb <sub>2</sub> O <sub>5</sub>	Ta <sub>2</sub> O <sub>5</sub> /Nb <sub>2</sub> O <sub>5</sub>	LiO	Rb <sub>2</sub> O	Cs <sub>2</sub> O
1	2	3	4	5	6	7	8	9
Type I. Microcline pegmatites								
1. Zone of inequigranular quartz- albite- microcline*	Biotite, muscovite, allanite	Always near borders and xenoliths	-	?	?	-	-	-
2. Zone of graphic quartz- microcline		Usually near borders, sometimes after zone 1	-	-	-	-	-	-
3. Zone of pegmatoid quartz- microcline	Tourmaline, muscovite, albite	After zone 1 or 2, less often near borders	-	-	-	-	-	-
4. Zone of blocky microcline I**	Quartz, muscovite, albite, large beryl prisms (on boundaries with blocks or cores of quartz)	Usually after zone 2 or 3, less often after zone 1	-	-	-	-	-	-
5. Zone of blocky quartz		In the center of veins	>0.03-0.05	-	-	-	-	-

Table 1 (Continued)

Zones (the name of a zone indicates its most characteristic structure and principal minerals)	Minerals of secondary importance and typomorphic minerals	Position in the pegmatite body	Typical content of rare elements, %					
			BeO	Ta <sub>2</sub> O <sub>5</sub> + Nb <sub>2</sub> O <sub>5</sub>	Ta <sub>2</sub> O <sub>5</sub> /Nb <sub>2</sub> O <sub>5</sub>	LiO	Rb <sub>2</sub> O	Cs <sub>2</sub> O
1	2	3	4	5	6	7	8	9
Type II. Albite-microcline pegmatites								
1. Zone of inequigranular quartz- albite-	Muscovite, tantalite-	Always near borders and	-	0.010-0.020	0.4-0.6	-	-	-
2. Zone of graphic quartz-	columbite	After zone 1 or at borders	-	-	-	-	-	-
3. Zone of apographic quartz-albite-	Muscovite, tourmaline, spodumene, tantalite-	After zone 1 or at borders	-	-	-	-	-	-
4. Zone of large sheets of muscovite***	columbite Albite, quartz, relicts of microcline	After zones 1 or 2	-	0.015-0.025	0.5-0.7	-	-	-

Table 1 (Continued)

Zones (the name of a zone indicates its most characteristic structure and principal minerals)	Minerals of secondary importance and typomorphic minerals	Position in the pegmatite body	Typical content of rare elements, %					
			BeO	Ta <sub>2</sub> O <sub>5</sub> + Nb <sub>2</sub> O <sub>5</sub>	Ta <sub>2</sub> O <sub>5</sub> /Nb <sub>2</sub> O <sub>5</sub>	LiO	Rb <sub>2</sub> O	Cs <sub>2</sub> O
1	2	3	4	5	6	7	8	9
4a. Zone of fine-grained albite with beryl	Muscovite, quartz, garnet, apatite, beryl, tantalite-columbite, relicts of microcline, bismuth minerals	After zones 1 or 2						
4b. Zone of coarse platy albite***	Quartz, muscovite, tourmaline, finely-crystalline tantalite etc.	Near borders on the hanging wall	0.12-0.16	0.015-0.025	0.5-0.7	-	-	-
5. Zone of blocky microcline I**	Quartz, Muscovite, albite	After zones 1 or 2, 3, 4, 4a, 4b	-	(0.030-0.040)	(1.5-2.0)	-	-	-
			-	-	-	-	to 1.1	-



Table 1 (Continued)

Zones (the name of a zone indicates its most characteristic structure and principal minerals)	Minerals of secondary importance and polymorphic minerals	Position in the pegmatite body	Typical content of rare elements, %					
			BeO	Ta <sub>2</sub> O <sub>5</sub> + Nb <sub>2</sub> O <sub>5</sub>	Ta <sub>2</sub> O <sub>5</sub> /Nb <sub>2</sub> O <sub>5</sub>	LiO	Rb <sub>2</sub> O	Cs <sub>2</sub> O
1	2	3	4	5	6	7	8	9
6. Zone of quartz-muscovite	Albite, cleve-landite, relicts of microcline, small crystals of light-green beryl, tantalite-columbite, bismuth minerals	Usually replaces zone 5, less often zones 1 or 2						
7. Zone of saccharoidal albite	Quartz, muscovite, garnet apatite, columbite	After zone 5 or 6	0.09-0.12	0.015-0.025	0.5-0.8	-	-	-
8. Zone of quartz-clevelandite-spodumene	Muscovite, montebasite, lithiophilite white sodium-lithium beryl, tantalite-columbite	After zone 7, less often after zone 5 or 6	-	0.020-0.030	0.5-0.8	-	-	-
			0.05-0.07	0.030-0.040	1	1.2-1.5	-	-

Table 1 (Continued)

Zones (the name of a zone indicates its most characteristic structure and principal minerals)	Minerals of secondary importance and typomorphic minerals	Position in the pegmatite body	Typical content of rare elements, %					
			BeO	Ta <sub>2</sub> O <sub>5</sub> + Nb <sub>2</sub> O <sub>5</sub>	Ta <sub>2</sub> O <sub>5</sub> / Nb <sub>2</sub> O <sub>5</sub>	LiO	Rb <sub>2</sub> O	Cs <sub>2</sub> O
1	2	3	4	5	6	7	8	9
9. Zone of fine platy albite with lepidolite, polylucite, tantalite and other rare metal minerals	Pink spodumene, pink muscovite, vorobyevite, pink or variegated tourmaline, tantalite, simpsonite, microlite, stibiotantalite	After zone 5 or 8	0.04-0.06	0.040-0.050	2 or more	1.2-1.5	to 1.0	to 1.3
10. Zone of scaly lepidolite	Albite, rarely quartz, tantalite, rubellite	After zone 8 or 9	-	0.050-0.070	3-5	1.0-2.0	-	-
11. Zone of blocky quartz ***	Spodumene	Always in the core	-	-	-	-	-	-
Type III. Albite pegmatites								
1. Zone of apographic quartz-albite	Muscovite, tourmaline, garnet, apatite, columbite	Always near borders or xenoliths	-	0.015-0.020	0.5	-	-	-

Table 1 (Continued)

Zones (the name of a zone indicates its most characteristic structure and principal minerals)	Minerals of secondary importance and typomorphic minerals	Position in the pegmatite body	Typical content of rare elements, %					
			BeO	Ta <sub>2</sub> O <sub>5</sub> + Nb <sub>2</sub> O <sub>5</sub>	Ta <sub>2</sub> O <sub>5</sub> / Nb <sub>2</sub> O <sub>5</sub>	LiO	Rb <sub>2</sub> O	Cs <sub>2</sub> O
1	2	3	4	5	6	7	8	9
2. Zone of saccharoidal albite	Quartz, muscovite, garnet, apatite, columbite, arsenopyrite	After zone 1 and at borders						
3. Zone of cleavelandite **	Quartz, muscovite, garnet, apatite, columbite, arsenopyrite, tantalite-columbite, beryl, lithiophilite	After zone 2; in gently-dipping pegmatites, at borders on the hanging wall	-	0.020-0.030	0.5-0.8	-	-	-
4. Zone of flaky (or scaly) muscovite	Albite, tantalite, small amounts of quartz	After zone 3, less often, after 2	0.30-0.50	0.030-0.040	1	-	-	-
5. Zone of blocky microcline II **	Quartz, albite, muscovite	After zone 3 or 4 but always before zone 6	-	0.040-0.060	2-3	-	-	-
			-	-	-	-	-	-



Table 1 (Continued)

Zones (the name of a zone indicates its most characteristic structure and principal minerals)	Minerals of secondary importance and typomorphic minerals	Position in the pegmatite body	Typical content of rare elements, %					
			BeO	Ta <sub>2</sub> O <sub>5</sub> + Nb <sub>2</sub> O <sub>5</sub>	Ta <sub>2</sub> O <sub>5</sub> /Nb <sub>2</sub> O <sub>5</sub>	LiO	Rb <sub>2</sub> O	Cs <sub>2</sub> O
1	2	3	4	5	6	7	8	9
6. Zone of blocky quartz			-	-	-	-	-	-
Type IV. Albite-spodumene pegmatites								
1. Zone of fine-grained quartz-albite	Tourmaline, garnet, apatite, holmquistite, columbite	Always near borders or xenoliths	-	-	-	-	-	-
2. Zone of quartz-albite-spodumene	Microcline**** muscovite, triphylite, sodium-lithium beryl, columbite	After zone 1	-	-	-	-	-	-
3. Zone of blocky quartz-microcline-spodumene****	Above minerals and albite	Patches in zone 2	>0.02-0.04	0.013-0.020	0.5-0.8	1.2-1.5	-	-

Notes.

\* Infrequently oligoclase occurs instead of albite.

Table 1 (Continued)

\* \* In the granite rare metal pegmatites there are two monomineralic microcline zones, I and II.

Besides occupying a different position, blocky microcline II differs from blocky microcline I in several features: it is more transparent, often contains euhedral pseudohexagonal crystals or well formed individual crystal faces, clearly defined grid structure and a minimum content of perthitic intergrowth. It is characterized by the presence of a small but constant amount of albite (15-16%). It is always less albitized; it is never associated with large prismatic beryl which is so typical of blocky quartz-microcline I.

\* \* \* These zones are never found together in a pegmatite but proxy for each other.

\* \* \* In some veins this zone is preceded by a zone of blocky microcline II.

Sometimes the position of this zone is taken by quartz-cleavelandite-spodumene zone.

Microcline almost without perthitic intergrowth.

Moreover, a careful study of the rare metal mineralization of the individual zones in a large number of pegmatites indicates that the content of rare minerals in a given zone in different pegmatites is very similar (Table 1). The beryllium content in the blocky quartz-microcline zone of scores of pegmatites of the Altai Mountains usually ranges from 0.2 to 0.4%. The lithium oxide content in the quartz-albite (or cleavelandite) - spodumene zone, not only in the pegmatites investigated by the author but also in those described in the literature [9, 10], amounts to 1.2 - 1.5%. Fig. 1 shows that there is also a similarity in the content of Ta and Nb, but

a less pronounced one because of the extreme irregularity of distribution of these elements.

It should be noted in this connection that the character of distribution of the rare elements and the character of their behavior with increasing depth are definite in each zone. For example, in the blocky quartz-microcline zone, beryllium is very irregularly distributed and its content usually diminishes down dip, becoming non-economic at a depth of 10 to 30 m. In the zone of fine-grained albite, on the contrary, beryl is more regularly distributed and is found at a depth of several hundred meters without diminishing noticeably in amount.

Table 1 shows striking differences in the distribution of rare elements. Among the different zones found in the investigated pegmatites, tantalite-columbite (Ta and Nb) is found in considerable

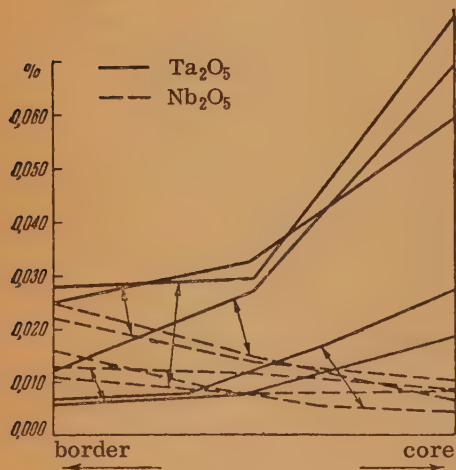


Fig. 1. Variation in the content of  $Ta_2O_5$  and  $Nb_2O_5$  from the borders to the core. Zones without ore (microcline) and quartz cores are omitted.

Note: Comma represents decimal point.

amounts in 14 zones, beryl (Be) in 8, spodumene (Li) in 4, rubidium (R6) in 2, and pollucite (Cs) in only one. Moreover, pollucite is characteristically restricted to the zone of fine-grained platy albite developed next to the quartz core, or if the latter is absent, forming the innermost part of the vein. Spodumene, in most cases, is also found either in the pegmatite core or in the zones adjacent to it.

Beryl occurs not only in the cores of pegmatite bodies but also in the intermediate zones. In the albite-microcline pegmatites, beryl is usually found in large amounts in one of the outer zones-- the zone of fine-grained albite. Finally, tantalite-columbite is developed in the central, intermediate and even in the border albite and mica zones.

The broadest range of distribution (from border to core) is shown by



columbite-tantalite; the range of beryl is somewhat narrower. When the concentration of lithium is low, the range of distribution of spodumene becomes considerably narrower. Pollucite has the narrowest range of all.

Naturally, the cause of this regularity must be sought in the properties of the rare elements entering into the different minerals. If these elements are listed in the order of decreasing range of distribution, the sequence will correspond exactly to the decreasing energy of their ions, as can be seen by comparing their EK values and ionic potentials with the number or zones containing substantial amounts of the element in question (Table 2).

Table 2

The Dependence of the Range of Distribution of Rare Elements on Their EK Values and Ionization Potentials

Elements	Ionization potential	<u>EK</u>	Number of zones containing the element	Ratio of the content of an element in the central zone to its content in the outer zones (for rich veins)
Ta	~ 55	12.2	14	up to 4
Nb	~ 50	12.2	14	0.3-0.8
Be	18.12	2.65	8	0.5-1
Li	5.36	0.74	4	~ 1
Rb	4.16	0.43	2	3-4
Cs	3.87	0.42	1	up to 13

As discovered by Fersman [7], this illustrates the dependence of the sequence of crystallization of minerals on the magnitude of their EK values: the greater this value the earlier the mineral forms.

It is well known that the crystallization of a given substance at a given temperature and pressure requires a perfectly definite minimum concentration of the substance. The elements whose ionic energies are greater can form independent minerals at relatively low concentration, while the elements with small ionic energies can form independent minerals only when their concentration is relatively high. Tantalum and niobium have high ionic energies, and although their concentration may be relatively low, they form an independent mineral, tantalite-columbite, in the very beginning of the pegmatitic process. On the other hand, cesium, an element of low energy, cannot form an independent mineral until it becomes enriched in the solution during the process of fractional crystallization, because its initial concentration is insufficient to form pollucite. Pollucite, therefore, does not appear in the earlier zones but crystallizes only in the later, central zones of pegmatites.

In accordance with the law of mass action, the initial concentration of rare elements in pegmatite magma has a very strong effect on the distribution of minerals containing rare metals through the bulk of a pegmatite body, predetermining their formation in only one or in several zones.

When the initial concentration of a rare element is high, its minerals begin to crystallize earlier in the outer zones; when the concentration is low, they crystallize later in zones nearer the center of the vein. In microcline pegmatites containing relatively little beryllium (as a rule, not more than 0.01 - 0.02% for the whole vein), beryl is always found in the inner zones along the boundaries between microcline and quartz. On the other hand, in albite-microcline pegmatites, usually containing 0.04 - 0.05% BeO, beryl occurs not only in the inner zones but also outside the microcline zone. However beryl is not extended out to the zones of graphic and apographic pegmatite (Table 1, Figs. 2, 3). In albite pegmatites with still higher BeO content (0.10 - 0.20%), beryl crystals often grow from the contact with the enclosing rock. No less characteristic in this connection is the behavior of lithium, as is well illustrated by the example of albite-microcline pegmatites containing variable amounts of lithium. When the concentration of

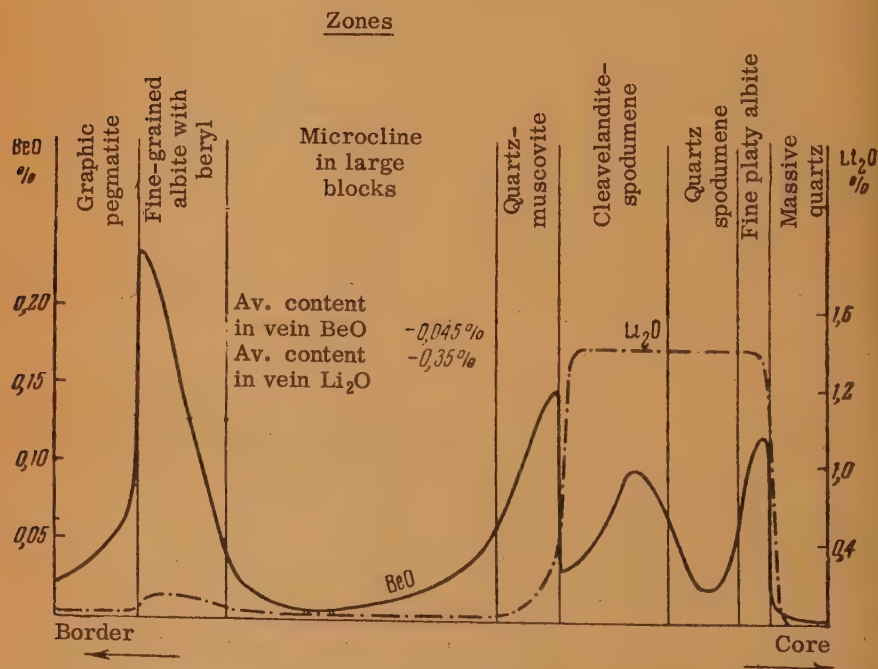


Fig. 2. Variation in the content of BeO and  $\text{Li}_2\text{O}$  from the borders to the core

Note: Comma represents decimal point.

lithium in the melt is low (about 0.1 - 0.35%  $\text{Li}_2\text{O}$  in the vein as a whole), it is found only in the inner zones (Fig. 2), whereas if its concentration is higher (up to about 1%  $\text{Li}_2\text{O}$ ), spodumene occurs in both the inner zones and outside of the zone of monomineralic microcline (Fig. 3). In albite-spodumene

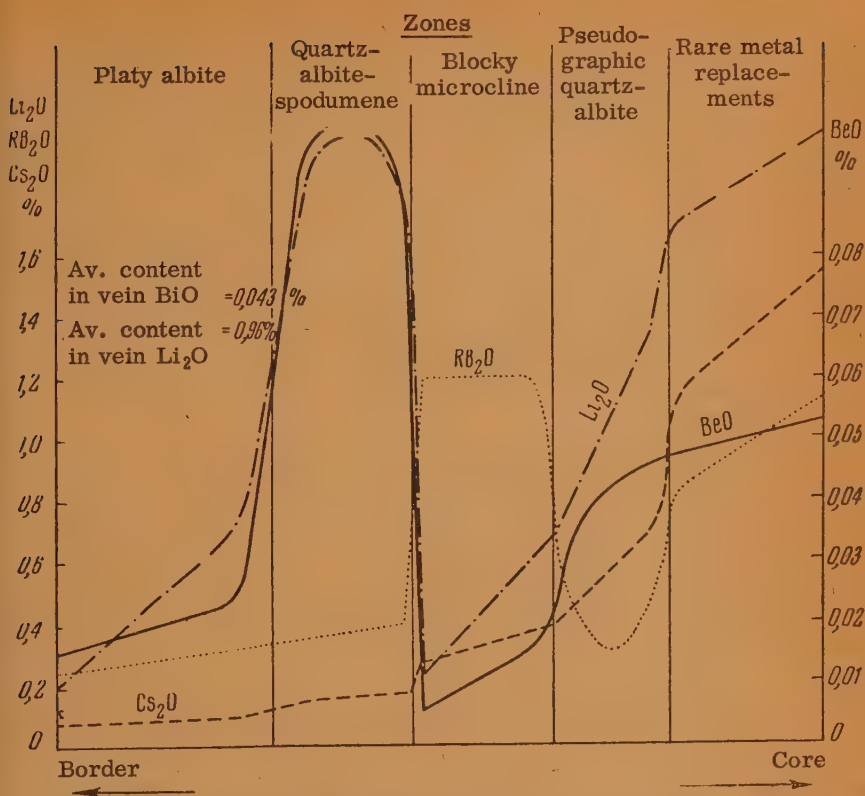


Fig. 3. Variation in the content of  $\text{BeO}$ ,  $\text{Li}_2\text{O}$ ,  $\text{Rb}_2\text{O}$  and  $\text{Cs}_2\text{O}$  from the borders to the core

Note: Comma represents decimal point.

pegmatites where the concentration of lithium reaches 1.5%  $\text{Li}_2\text{O}$ , spodumene crystals are often found near the borders of the pegmatitic body and throughout its mass.

Of great practical and theoretical interest is the analysis of the change in the content of rare elements throughout the mass of the pegmatite body. The average content of rare elements in the different zones of albite-microcline and albite pegmatites was calculated using the abundance data of Ya. Kh. Eseev, M. P. Zueva, M. V. Kuz'menko, V. A. Khvostova and those of the writer. The results are shown graphically in Figs. 1, 2 and 3. To make the graph easier to read, the graphic quartz-microcline and monomineralic massive microcline zones, which are practically devoid of rare elements, are omitted from Fig. 1, and only the albite and mica zones are shown, which as a rule contain some of the rare elements.

Comparison of the content of rare elements in the outer, intermediate and inner zones clearly shows differences in the behavior of different



elements. The  $\text{Nb}_2\text{O}_5$  content usually decreases from the borders to the core, being 0.025 - 0.010% in the outer zones and 0.010 - 0.006% in the inner (Fig. 1). The  $\text{Ta}_2\text{O}_5$  content, on the other hand, shows a strong tendency to increase from 0.006 - 0.025% in the outer zones to 0.020 - 0.070% in the inner. For this reason the Ta/Nb ratio always increases regularly from the borders to the core. This is apparently characteristic of all granite pegmatites and has been repeatedly mentioned in the literature [3, 4].

Increase in tantalum content in all pegmatites is more rapid than decrease in the niobium content, and for this reason the sum of tantalum and niobium pentoxides increases from 0.015 - 0.030% to 0.050 - 0.075% from the borders to the core of veins.

It is interesting to note that with the sum of tantalum and niobium pentoxides ranging from 0.015 to 0.030% (for the whole vein), which is characteristic of the pegmatites investigated, the behavior of tantalum and niobium remains the same and does not depend on their concentration (within the given limits).

However, the behavior of beryllium depends strictly on its concentration. In the albite-microcline pegmatites, usually containing 0.04 - 0.05% BeO (for the whole vein), beryl is found in two places: 1) in the zone of fine-grained albite preceding the zone of blocky microcline and 2) in the albite and mica zones following the zone of blocky microcline (Table 1). The BeO content in the fine-grained albite zone is several times higher (0.10 - 0.16%) than the inner albite zones, usually containing not more than 0.05 - 0.06% BeO (Fig. 2). Therefore, the BeO content decreases from the borders to the core in beryllium-rich pegmatites. On the other hand, beryllium-poor pegmatites, - for example in microcline pegmatites, with BeO content from 0.005 - 0.02% for the whole vein, - all beryl is concentrated in the central blocky quartz-microcline zone. In this case the BeO content may be said to increase towards the core (Table 1).

An equally clear dependence on concentration is shown by lithium. In the albite-microcline pegmatites with  $\text{Li}_2\text{O}$  content of about 0.35% and more (for the whole vein), spodumene and some other lithium minerals occur both preceding and following the zone of blocky microcline. The lithium content may be nearly the same in both places (Fig. 3). When the lithium content in the veins is low, spodumene is developed mainly in the inner zones near the zone of blocky microcline (Fig. 2).

Rubidium and cesium in relatively large amounts are found only in the albite-microcline pegmatites, the other types of pegmatites carrying only clarke amounts of these elements. The character of distribution of Rb and Cs was studied in several veins of the albite-microcline type. Because in all veins investigated the behavior of rubidium and cesium was the same, their distribution is discussed below on the basis of a special detailed study of one of the veins (Fig. 3).

All rubidium is present in pegmatites in the dispersed state. The minerals most strongly enriched in Rb in the veins investigated [6] are microcline (0.3 - 1.55%, rarely 2.80%), lepidolite (0.2 - 2.7%), pollucite (0.14 - 0.58%), pink tourmaline (up to 0.72%) and pink muscovite (up to 0.7%). Inasmuch as microcline is the most abundant of these minerals and forms its own intermediate zone, while the rest of the minerals are developed only in the central replacement zone, the curve of rubidium content shows two maxima (Fig. 3). One occurs in the zone of blocky microcline and another in the central albite zone containing lepidolite, pollucite, pink muscovite, rubellite and late microcline. On the whole, in spite of the presence of the

Table 3  
Rubidium and Cesium Content in Microcline from Different Zones\*

Zones (in order of their position from the borders to the core)	Number of samples	Rubidium, %		Number of samples	Cesium, %	
		range	average		range	average
Zone of granite pegmatite	4	0,16—0,60	0,36	2	0,016—0,045	0,031
Zone of apographic quartz-albite-microcline	6	0,35—1,40	0,91	3	0,058—0,160	0,097
Zone of blocky microcline	8	0,35—2,80	1,07	4	0,055—0,230	0,133
Zone of rare metal replacement	2	>> 1—1,60	1,60	1	0,120	0,120

\* Analyses were made by T. F. Borovik-Romanova (GEOKHi Acad. Sci. USSR) on material provided by A. F. Sosedko. Some of the analyses for rubidium were made by L. I. Sazhina (IMGRE Acad. Sci. USSR) on the author's material

Note: Comma represents decimal point.

second maximum in the intermediate zone (1.14%), the  $\text{Rb}_2\text{O}$  content does not show any significant increase from the border (0.32%) to the inner (0.96%) zone. The general tendency towards concentration of rubidium in the inner parts of the veins is manifested also in the increase in its content in samples of microcline taken at increasing distances from the borders (Table 3). The same phenomenon is observed in the case of tourmaline, muscovite, spodumene and other minerals.

The increase in  $\text{Cs}_2\text{O}$  content from the borders to the core is still sharper, changing from 0.10% in the outer to 1.34% in the inner zones (Fig. 3). In the three outer zones, where Cs is present in the dispersed state [6], its content increases slowly in the different rock-forming minerals. Then, in the pseudo-graphic quartz-albite zone, where pollucite begins to appear, the content of  $\text{Cs}_2\text{O}$  grows rapidly, and in the central zone of rare metal replacement, rich in pollucite, it reaches its maximum. As in the case of rubidium, the amount of cesium dispersed in microcline and other minerals increases with increase in distance from the borders (Table 3) owing to the increase in its concentration towards the later stages of the pegmatitic process.

Thus, for the pegmatites investigated the initial concentrations of the oxides in the melt amounts to 0.005 - 0.025% for  $\text{Ta}_2\text{O}_5$ , 0.009 - 0.020% for  $\text{Nb}_2\text{O}_5$ , 0.005 - 0.240% for  $\text{BeO}$ , 0.005 - 1.500% for  $\text{Li}_2\text{O}$ , 0.05 - 0.60% for  $\text{Rb}_2\text{O}$  and 0.005 - 0.400% for  $\text{Cs}_2\text{O}$ . The content of tantalum, rubidium and cesium always increases markedly from the borders to the core; the content of niobium decreases; and the behavior of beryllium and lithium is irregular. When the concentration of the last two elements is low, their average content increases as the core is approached; when it is high, their content decreases or remains the same in the inner and outer zones.

Such diverse behavior of the rare elements is probably due to the differences in the energies of their ions, for the content of the elements with small EK values and ionization potentials (Rb, Cs) is higher near the center, while the content of elements with high ionic energies (niobium and, in rich veins, beryllium) is higher in the outer zones. This relationship is especially clearly seen when the ionic energies are compared with the ratios of the contents of the rare elements in the central and outer zones (Table 2). A rather strict dependence is then observed: the smaller the value of EK and of the ionization potential of a rare element, the greater its enrichment in the center of a vein. Tantalum is an exception to this rule. This element has a high ionic energy, but it quite definitely accumulates in the central zones, owing, apparently, to its presence in the form of stable complex compounds capable of remaining in solution for a long time.

These regularities in the distribution of rare elements in rare element pegmatites with zonal structure serve as a weighty argument in favor of the view expressed by Fersman [8] and other investigators who believe that the main mass of rare elements is present in the pegmatite melt from the very beginning of the formation of pegmatites. The idea that pegmatites form by fractional crystallization of the pegmatitic melt provides a simple explanation of these regularities, which are no more than the logical consequence of the process.

On the contrary, the hypothesis of later introduction of the rare elements into pegmatites recently developed by V. D. Nikitin [5] and other authors does not explain the regular distribution of the rare elements but suggests, rather, that no such regularity can be expected, because the channels through which the ore-bearing solutions circulate, whether they are



tectonic or contraction fractures, can appear in any part of the pegmatite, near its borders or in its core.

### Summary

The above discussion leads to the conclusion that the distribution of the rare elements in the rare metal granite pegmatites is determined 1) by the spatial distribution of the principal rock-forming minerals, in other words, by the zonal structure of the pegmatites; 2) by the EK values and ionization potentials of the rare elements (Table 2); 3) by their initial concentration in the pegmatite melt; 4) by the distribution of the minerals capable of capturing a given rare element; and 5) by the chemical composition of the medium relative to point 5, when large amounts of the rare earths are present, beryllium for example becomes strongly dispersed [1] and the character of its distribution is modified.

### REFERENCES

1. Beus, A.A. (1956). *Geokhimiya*, No. 1.
2. Vlasov, K.A. (1952). *Izvestiya, ser. geol.*, No. 2, Izd. Akad. Nauk SSSR.
3. Ginzburg, A.I. (1956). *Geokhimiya*, No. 3.
4. Cameron, E.N., R.H. Jahns et al (1951) *Vnutrennee Stroenie Granitnykh Pegmatitov* (Internal structure of granitic pegmatites). *Izd. in. lit.*
5. Nikitin, V.D. (1956). *Zap. Vs. min. obshchestva*, 86, No. 1.
6. Solodov, N.A. (1958). *Geokhimiya*, No. 8.
7. Fersman, A.E. (1937). *Geokhimiya* (Geochemistry), v. 3, Goskhimtekhnizdat, L.
8. Fersman, A.E. (1940) *Pegmatity* (Pegmatites), v. 1, Izd. Akad. Nauk SSSR, M.
9. Davies, J.F. (1956). *Canad. Mining J.*, 74, No. 4.
10. Rye, E.G. (1956). *Canad. Mining J.*, 74, No. 4.

Received for publication  
January 5, 1959.

# GEOCHEMISTRY OF CADMIUM IN THE ALMALYK AND ALTYN-TOPKAN MINERALIZED AREAS OF THE KARAMAZAR REGION

S. T. BADALOV and M. P. ENIKEEV  
Geological Institute, Academy of Sciences,  
Uzbek SSR, and the V.I. Lenin University  
of Middle Asia, Taskent

The main features of the geochemistry of cadmium in ore deposits have been described in numerous papers by A. E. Fersman [15], S. S. Smirnov [13, 14], V. F. Alyavdin and A. G. Betekhtin [2], F. I. Abramov and A. K. Rusanov [1], and others. However, because of the scarcity of quantitative data on the distribution of cadmium in the minerals of individual mineral deposits, it has not been possible to determine some of the characteristics of its distribution.

Our paper presents data on the geochemical behavior of cadmium under hypogene and supergene conditions obtained from a mineralogical and geochemical investigation of two adjacent mineralized areas in the Karamazar region, the Altyn-Topkan and the Almalyk. Data from the neighboring ore deposits of the Karamazar region and published data from other ore deposits in the USSR and abroad were used for comparison.

1. Of the investigated ore deposits, the Almalyk (studied by S. T. Badalov) and the Altyn-Topkan (studied by M. R. Enikeev) are the most interesting of all Karamazar deposits, not only because they contain the greatest variety of ores (molybdenum, copper-molybdenum, polymetallic, gold, and fluorite-polymetallic) but also because the maximum range of cadmium content in a given mineral is found here, for example, from 0.08 to 1.91% in the sphalerites. The cadmium content in sphalerites in all other mineralized areas lies within these limits.

Before discussing the geochemistry of cadmium, it is necessary to give a brief description of the geological setting of the investigated ore deposits.

The Almalyk area contains sedimentary, effusive, and intrusive rocks. Among the sedimentary rocks, referred to the Upper Devonian and Carboniferous, the carbonate rocks are predominant (limestones and dolomites). The most widely distributed intrusives are syenites and syenite-diorites cut by granodiorite porphyry stocks. All known ore bodies of the region lie near large faults. The copper-molybdenum and gold ore bodies are related to the intrusive, and partly to the effusive rocks; the polymetallic ores lie in the carbonate rocks and very seldom in the igneous rocks.

The Altyn Topkan mineralized area is also composed of rocks of different origin: Silurian schists, Upper Devonian and Carboniferous carbonate rocks, Upper Paleozoic acid and intermediate effusives and dominantly siliceous intrusives.

The polymetallic ores of the region are related to faults of different magnitude, which cut the skarn zones near contacts between intrusive and carbonate rocks, effusive rocks and, less frequently, metamorphic and intrusive rocks.

A detailed study of the Almayk ore deposit provided geological, mineralogical, and geochemical criteria for dividing the process of mineralization into five phases, each usually consisting of several subphases.

The age sequence of these phases is as follows:

- I -- the phase of pre-ore alteration of the country rocks,
- II -- the phase of copper-molybdenum and gold mineralization,
- III -- the polymetallic phase,
- IV -- the phase of gold mineralization, and
- V -- the rare metals phase.

Our paper presents data on the distribution of cadmium in the minerals of the copper-molybdenum, polymetallic, and gold phases of the Almayk mineralized area, and the polymetallic phase of the Altyn-Topak area. Cadmium was determined polarographically and chemically in the laboratory of the "Uzgeolrazvedka" organization and at the Geological Institute of the Uzbek Academy of Sciences (analysts: V. A. Moskvitina, P. L. Prikhid'ko, and V. V. Prasalova). The accuracy of cadmium determination was 0.005 - 0.01%.

The discussion of the distribution of cadmium will begin with the earliest phases. The earliest subphase of the copper-molybdenum-gold phase was marked by the formation of quartz-wolframite-molybdenite veins, followed by quartz-molybdenite veins and veinlets, and finally by the deposition of chalcopyrite, galena, sphalerite, and other minerals.

Tables 1 and 2 show the content of cadmium in the sphalerites from the copper-molybdenum deposits of the Almayk mineralized area and from different regions of the USSR and USA.

Table 1

Cadmium Content in Sphalerites from the Almayk  
Copper-Molybdenum Deposit

Variety of sphalerite	Number of samples	Range of variation in cadmium content, %	Average cadmium content, %	Subphase of mineralization
Marmatite	1	0.08	0.08	Tungsten-molybdenum Molybdenum-copper "
Marmatite	2	0.15 - 0.19	0.17	
Cleiothane	4	0.12 - 0.19	0.15	
Sphalerite	5	0.20 - 0.26	0.23	
Cleiothane	3	0.24 - 0.27	0.25	
Average			0.20	



Table 2

Cadmium Content in Some Deposits of the USSR and USA

Cadmium content, %	Iron content, %	Locality and region	Sampling locality or deposit
0.11	20.54	Takhtarvumchorr, Kola Peninsula	Molybdenum deposit [2]
0.10	19.40	Yukspor, Kola Peninsula	Lovchorrite dike [2]
tr. to 0.09	10 to 16	Franklin, N. J., U. S. A.	Franklinite deposit [24]
0.39	14.69	Stalinskoe, Primor'e region	With arsenopyrite, cassiterite etc. [2]
0.027	8.80	Bukuka, Transbaikalia	Wolframite greisen [2]
up to 0.14	tr. to 3.24	Karpushinskoe, Urals	Chalcopyrite deposit [18]
n.d.	0.22	Lovozero massif, Kola Peninsula	Alkalic rocks [2]
traces	traces	Franklin, N. J., U. S. A.	Franklinite deposit [24]
0.27 - 0.37	"	Kedabek, Chiragidzer, Lesser Caucasus	Pyrite deposit [19]
0.1	"	Kounrad, KazSSR	Copper-molybdenum [7]
0.005 - 0.1	"	Yavlenskoe, Eastern Transbaikalia	With tourmaline, cassiterite and pyrite [17]
0.01 - 0.07	"	E. Arshinskoe, Urals	Pyrite-polymetallic mineralization [11]

According to the data of Table 2, the sphalerites from these regions are very close in their cadmium content to the sphalerites of the Almalyk copper-molybdenum phase of mineralization (see Table 1). It is interesting that in each type of mineralization within a given geochemical province the variation of the cadmium content in sphalerites is small and almost independent of the iron content.

2. The sphalerites of polymetallic deposits in the mineralized areas under discussion contain larger amounts of cadmium than the sphalerites of copper-molybdenum deposits. The cadmium content (average) ranges from 0.30% in the Kurgashinkan group (Almalyk area) to 1.10% in the Sardob deposit (Altyn-Topkan area). The large number of chemical determinations of cadmium presented in Table 3 gives a schematic picture of its distribution in the different deposits of the southwestern Karamazar region. The data for several other ore deposits of the USSR (Lesser Caucasus, South Osetia, Nagol'nyi Kryazh) are given for comparison.

Clearly the cadmium content in the sphalerites of the polymetallic deposits of the Karamazar region is very high. The Almalyk area, lying a little to the side of the main ore zone of the Kuraminskii Mountains, has

Table 3

Cadmium and Iron Content in Sphalerites of Polymetallic Deposits of Western Karamazar and the Comparative Data on the Other Regions of the USSR

Number of samples analyzed for Cd	Cadmium content, % (from-to)	Average cadmium content, %	Iron content, % (from-to)	Deposit or mineralization	Mineralized area	Author
24	0.20-0.42	0.25	0.68-10.5	Kurgashinkan	Almalyk	S. T. Badalov
2	0.26-0.42	0.34	n. d.	Nakpai	"	M. Ismailov
3	0.42-0.48	0.45	"	Kantrangi	"	S. T. Badalov
22	0.81-1.91	1.10	"	Sardob	Altyn-Topkan	M. R. Enikeev
31	0.47-1.11	0.72	2.50-10.6	Tash-Geze	"	"
23	0.62-1.36	0.87	1.10-3.4	Main ore zone	"	"
14	0.47-0.79	0.72	n. d.	North, group of ore bodies	"	"
5	0.38-0.53	0.45	"	Aigyr-Bulak	"	"
2	0.50-0.59	0.54	"	Chashly	"	"
8	0.62-1.54	1.00	2.0-3.3	Central Kansai	Kansai	Z. M. Protod'yakonova
4	0.85-1.30	0.99	3.0-6.8	Shevchukovka	"	"
4	0.60-1.15	0.87	n. d.	Ak-Tash	"	"
13	0.55-1.04	0.80	"	Kurusai I, II, III	Kurusai	M. I. Moiseeva
7	0.66-0.78	0.72	0.3-5.3	Uch-Ochak	Takelii	"
2	0.58-0.70	0.64	4.0-4.6	Sassyk-Sai	"	"
3	0.62-0.74	0.66	4.1-8.5	West. Kaptarkhana	"	"
59	0.20-0.39	0.26	tr. to 14.47		Rudnyi Altai	B. I. Veits [6]
6	0.21-0.82	0.5	0.16-2.33	Mekhmaninsk group	Lesser Caucasus	G. Kh. Efendiev [19]
2	n. d.	-	0.08-2.42	Verkh. Kvaisa	South Osetiya	V. P. Pankov [12]
4	0.35-0.77	0.60	0.22-2.15		Nagol'nyi Kryazh	A. A. Yakzhin [20]

sphalerites of relatively low cadmium content (about 0.3% on the average).

It should be noted that in each mineralized area there is a definite range of variation in the cadmium content of the sphalerites. Usually the maximum content is twice the minimum.

Some variations are due to the genetic peculiarities of the individual deposits (fluorite-polymetallic, etc.). For instance, in the fluorite deposit at Chashla, the average cadmium content in sphalerite is 0.54%, but in the neighboring Glavnaya zone of the Aityn Topkan area, it is 0.87%.

Interesting from the geochemical point of view are such facts as the relatively high cadmium content in the sphalerites from the phosphorite concretions of Podolia, reaching 0.59%, according to E. P. Furman [16], in the brunnkite from Truskavetz (0.76%) and especially in the brunnkite from Tserkapukio (2.08%) according to E. K. Lazarenko's data [10], and the absence of cadmium from the colloform sphalerites of hydrothermal origin from Verkhnyaya Kvaisa [12]. These facts may be very important in the elucidation of the geochemistry of cadmium, but the published data on them are still very scant.

The available data indicate that in polymetallic deposits also there is no definite relation between the cadmium and iron content in sphalerites. Among the numerous analyzed sphalerites from each deposit, there were varieties ranging from marmatite to cleiophane, but their cadmium content varied within rather narrow limits.

3. To discover all the characteristics of behavior of cadmium during the process of ore deposition, it is necessary to investigate other minerals besides sphalerite, first of all, the zinc-bearing minerals. No systematic studies of this kind have been made so far, and the literature contains very few data on the cadmium content in ore minerals other than sphalerite. The behavior of cadmium in sphalerite throws light on its behavior in other ore minerals of a deposit. The absence of cadmium from sphalerite, or the very low content of it, indicates that the mineralized area is poor in cadmium, as is the case with the Franklin deposit [24].

Among the ore minerals containing cadmium, tetrahedrite should be noted. Unfortunately, data on cadmium in tetrahedrite are lacking in the majority of published works [8 and others]. Table 4 presents the data on the cadmium content in zincian tetrahedrite available to the authors.

In all cases the ratio of cadmium to zinc in tetrahedrite is several times as high as in the sphalerites richest in cadmium from the same deposits.

Table 4

Cadmium Content in Tetrahedrites of Karamazar and Rudnyi Altai

Mineral	Cadmium content, %	Zinc content, %	Locality	Mineralized area	Author
Sandbergerite	0.24	10.0	Lashkerek	Lashkerek	R. L. Dunin-Barkovskii
Tetrahedrite	0.11	3.39	Gainak-Kan	Takeli	M. I. Moiseeva
"	0.08	6.0	Zyryanovsk	Rudnyi Altai	B. I. Veits [6]
"	0.2	7.94	Sokol'noe	"	"



Thus, in the sphalerites of Lashkerek, the cadmium content is 0.7%, in those of Takeli 0.6 - 0.7%, and in the sphalerites of Rudnyi Altai, 0.2 - 0.3%. These data indicate that the occurrence of cadmium in tetrahedrite cannot be ascribed to a mechanical admixture of sphalerite, and no sphalerite inclusions were discovered in tetrahedrite by the usual methods of investigation. The following explanation is the most likely: tetrahedrite, which because of its assemblage of admixed elements is the best indicator of the primary composition of the ore fluid, concentrates cadmium together with zinc when it crystallizes from a solution with high cadmium content. Under these conditions, if the solution contains excess of copper, antimony, and arsenic, the simultaneous entry of zinc and cadmium into the tetrahedrite lattice is more advantageous energetically than the formation of independent cadmium sphalerite.

4. A considerable number of published papers are devoted to the behavior of cadmium in the oxidized zone of polymetallic deposits [3, 4, 9, 13, 23 and others], but certain features in the behavior of cadmium remain little known. In the hypogene processes cadmium is localized mainly in sphalerite and partly in Zincian tetrahedrite, but in the oxidized zone the geochemistry of cadmium is different from that of zinc.

Cadmium minerals are very rare and usually occur only in the oxidized zone of polymetallic deposits. Only a few cadmium minerals are known: greenockite, otavite, cadmium oxide and cadmoselite [5]. Greenockite is less rare than the other cadmium minerals, and usually occurs in fractures in sphalerite. Very rarely, hydrothermal greenockite is found [8]. The presence of greenockite is an indication of high concentration of cadmium in a sphalerite deposit. It is very natural, therefore, that greenockite has been found in large amounts in the Altyn-Topkan deposits but not in the Almalayk area.

S. S. Smirnov [13] write that "the behavior of cadmium in the oxidized zone is identical with that of its analogue -- zinc... cadmium sulfate, which forms from the oxidation of zinc, is very easily soluble and in general behaves exactly like zinc sulfate." He noted also that the distribution of cadmium content in the different types of oxidized zinc ores, hemimorphite, smithsonite and others, remains uninvestigated.

The data given in Table 5 fill this gap to some extent. In compiling this table, all available determinations of cadmium in the minerals of the oxidized zone from the USSR and foreign deposits were used.

The largest cadmium concentration, according to Table 5, apart from the independent cadmium minerals, which do not form economic deposits, is found only in smithsonite and, very rarely, in calcite.

In many deposits, smithsonite is the only cadmium-bearing mineral of practical importance.

Table 5 shows also that smithsonites are somewhat richer in cadmium than the sphalerites from the same deposits. Thus, while thirteen analyses of sphalerites from the Takeli deposit (see Table 3) give average cadmium content of about 0.65% (range of content: 0.58 to 0.78%), seven analyses of smithsonites from the same deposit give average cadmium content of 1.13% (range of content: 0.82 to 1.61%). In this case, even the lowest cadmium content in smithsonite is higher than the maximum content in sphalerite. It is characteristic that the cadmium content in the smithsonites of Altai is related to their color, which, in its turn, depends on their iron content. In the brown varieties from the Zyryanovskoe and Chagirskoe deposits of Altai, cadmium occurs in traces, while in the more lightly colored varieties its amount is higher. It is known that monheimite forms

Table 5  
Cadmium Content in the Minerals of the Oxidized Zone in Some USSR and Foreign Deposits

Number of samples and sample number	Mineral	Range of cadmium content, %	Average Cd content, %	Locality and region	Author
590	Smithsonite	-	0.67	Aigyr-Bulak, Karamazar	M. P. Enikeev [9]
345	"	-	0.45	" "	"
3130	"	-	0.57	Main ore zone, Altyn-Topkan	"
7	"	0.82-1.61	1.13	Takeli, Karamazar	M. I. Moiseeva
2	"	0.31-0.43	0.37	Taininskoe, Transbaikalia	S. S. Smirnov [14]
7	"	0.20-0.50	0.30	Zyryanovsk, Altai	G. P. Bolgov [4]
1	"	-	0.64	Chigir, Altai	"
3	"	0.14-0.35	0.26	Zolotushinsk	"
1	"	-	2.70	Laurium, Greece	C. Doelter [22]
2	"	0.90-1.06	0.98	Morning Sta., Ark.	"
1	"	-	0.63	Marion Co., Ark.	"
2	"	tr. 0.05	0.03	Broken Hill, Rhodesia	J. Dana [21]
1	"	-	0.16	Kelly mine, N. M.	C. S. Hurlbut [23]
255	Goslarite	-	0.05	Altyn-Topkan, Karamazar	J. Dana [8]
349	Calcite	-	0.50	Aigyr-Bulak, Karamazar	M. P. Enikeev [9]
342	Calcite	-	0.11	" "	"

directly from oxidation of sphalerite, while the purer varieties of smithsonite are products of redeposition. The high cadmium content is found only in the cryptocrystalline varieties of smithsonite, the well-crystallized varieties being usually devoid of it (Broken Hill [23]). Evidently, in this case the entry of cadmium into smithsonite depends on the character and intensity of the process of redeposition. It is probable also that in the presence if iron the possibility of cadmium entering into the structure of smithsonite is very limited.

Thus, the cadmium content is different in smithsonites of different generations. In the early ferroan varieties it is very low; later, during the deposition of colloform smithsonite, it reaches a maximum; and, finally, during recrystallization and repeated redeposition accompanied by the formation of single crystals, it decreases again (Fersman's principle of self-purification). Evidently the conditions of formation of colloform cryptocrystallization of smithsonite and otavite, especially as the two minerals have very similar crystal structure.

Of the other minerals containing cadmium, only goslarite and calcite deserve mention. A sparsely distributed goslarite from Altyn-Topkan [9] contains only 0.05% Cd. No cadmium was detected by the spectrograph in any of the other samples of goslarite, hemimorphite [3], sauconite, aurichalcite, and other zinc-bearing minerals; in other words, the content of it in these minerals is less than 0.001%.

Of great interest is the occurrence of cadmium in the calcites of the Aigyr-Bulak deposit, in which the content of it reaches 0.5%. The possibility of "endocryptic absorption of cadmium by calcium minerals" was pointed out by Fersman [15], who believed that from the "geochemical point of view, it is desirable to check all calcium minerals for cadmium." The presence of cadmium in calcite must be explained either by diadochic substitution of cadmium for calcium or by simultaneous crystallization of calcite and otavite in colloform cryptocrystalline structures. It should be noted that in the investigated calcites the content of zinc does not exceed hundredths of one percent.

The behavior of cadmium in the oxidized zone is considerably different from that of zinc. The absence of cadmium in all minerals of the zone but smithsonite is due to the fact that in the oxidized zone cadmium, besides occurring as the sulfide greenockite, occurs only as otavite, which is structurally very near calcite and smithsonite. It is very probable that cadmium enters into these minerals because otavite is isomorphous with them. Cadmium does not form any other compounds in the oxidized zone, and so is not found in zinc sulfates, zinc silicates, or other zinc compounds.

5. The following features in the behavior of cadmium are observed in the investigated mineralized areas. Under hypogene conditions, cadmium is concentrated mainly in sphalerite and, less often, in zincian tetrahedrite. The content of cadmium in sphalerite increases regularly as the temperature of the ore formation decreases, so that its maximum content is found in the latest sphalerites. The data cited here show that the cadmium content in sphalerites depends not so much on their iron content as on the type of ore deposit and the paragenesis of the ore minerals.

The neglected fact that zincian tetrahedrites have relatively high concentrations of cadmium is decidedly interesting.

To gain further knowledge concerning the behavior of cadmium, it is necessary to continue the investigation of ore minerals which may be expected to contain it, even though they contain no zinc (chalcopyrite, bornite, enargite, etc.).



It has been found that in the oxidized zone cadmium is definitely localized in the zinc carbonate, smithsonite, and to a very small extent in colloform calcite, but is practically absent from other zinc minerals.

## REFERENCES

1. Abramov, F.I. and A.K. Rusanov (1939) Spektroskopicheskoe Issledovanie Tsinkovykh Obmanok na Kadmii, Indii, Germanii i Gallii (Spectroscopic investigation of sphalerites for cadmium, indium, germanium and gallium). GONTI.
2. Alyavdin, V.F. and A.G. Betekhtin (1940) Sfalerit. Mineraly SSSR, t. II (Sphalerite. Minerals of the USSR, v. II), Izd. Akad. Nauk SSSR, p. 118.
3. Badalov, S.T. (1955). Zap. Uzbekist. otd. Vses. mineralog. ob-va, vyp. 8, p. 161.
4. Bolgov, G.P. and B.I. Veits (1957) Mineralogiya Polimetallicheskih Mestorozhdenii Rudnogo Altaya, t. II (Mineralogy of polymetallic deposits of Rudnyi Altai, v. II). Alma-Ata.
5. Bur'yanova, E.Z., G.A. Kovalev and A.I. Komkov (1957). Zap. Vses. mineralog. o-va, 2 seriya, ch. 86, vyp. 5, p. 626.
6. Veits, B.I. and I.V. Pokrovskaya (1957) Mineralogiya polimetallicheskih Mestorozhdenii Rudnogo Altaya, t. I (Mineralogy of polymetallic deposits of Rudnyi Altai, v. I). Alma-Ata.
7. Gazizova, K.S. (1957) Mednoe Mestorozhdenie Kounrad (The Kounrad copper deposit). Gosgeoltekhizdat, Acad. Sci. Kaz SSR.
8. Dana, J.D., E.S. Dana and C. Palache (1950) Sistema Mineralogii 1 (System of mineralogy, 1) Izd. Inostr. lit., p. 270.
9. Enikeev, M.R. (1955). Tr. Sredneaz. un-ta, vyp. 63, kniga 6, geol. nauki, p. 13.
10. Lazarenko, E.K. (1953). Mineralog. sb. No. 7, L'vovsk. geol. ob-va pri un-te, p. 85.
11. Osetrov, O.A. (1957) Metallurgiya i Tekhnologiya Tsvetnykh Metallov, Geologiya i Gornoe Delo (Metallurgy and Technology of nonferrous metals, their geology and mining) Tr. Mosk. in-ta tsvetn. met. i zolota, No. 27, p. 341.
12. Pankov, V.P. (1951) Zap. Vses. mineralog. o-va, 2 seriya, ch. 80, vyp. 1.
13. Smirnov, S.S. (1936) Zona Okisleniya Sul'fidnykh Mestorozhdenii (Oxidized zone of sulfide deposits). ONTI p. 242.
14. Smirnov, S.S. (1955) K Mineralogii Nekotorykh Polimetallicheskih Rud Zabaikal'ya. Izbr. Trudy (Mineralogy of polymetallic ores of Transbaikalia. Selected works) Izd. Akad. Nauk SSSR, p. 18.
15. Fersman, A.E. (1939) Geokhimiya, t. IV (Geochemistry, v. IV), p. 195.
16. Furman, E.P. (1953). Mineralog. sb. L'vovsk. geol. o-va pri un-te, No. 7, p. 97.
17. Chitaeva, N.A. and F.I. Vol'fson (1957) Metallurgiya i Tekhnologiya Tsvetnykh Metallov, Geologiya i Gornoe Delo (Metallurgy and Technology of nonferrous metals, their geology and mining) Tr. Mosk. in-ta tsvetnykh met. i zolota, No. 27, p. 358.
18. Shadlun, T.N. (1941) Sfalerit. Mineralogiya Urala, t. II (Sphalerite. Mineralogy of the Urals, v. II) Izd. Akad. Nauk SSSR, p. 184.

19. Efendiev, G. Kh. (1957) *Gidrotermal'nyi Rudnyi Kompleks Severo-Vostochnoi Chasti Malogo Kavkaza* (Hydrothermal ore complex of the northeastern part of the Lesser Caucasus). Izd. Akad. Nauk. AzSSR, Baku.
20. Yakzhin, A. A. (1945) *Sovetskaya geologiya*, No. 8, p. 29.
21. Dana, J. D. (1909) *The system of mineralogy*, New York.
22. Doelter, C. (1912) *Handbuch der Mineralchemie*, Band I.
23. Hurlbut, C. S. (1954). *Amer. Mineralogist*, 39, 1, p. 47.
24. Palache, C. (1935) *The minerals of Franklin and Sterling Hills, Sussex County, New Jersey*. U. S. Geol. Survey Profess. Paper 180.

Received for publication  
January 10, 1958.

# INDIUM IN SOME TIN DEPOSITS OF YAKUTIA

V. V. IVANOV and N. V. LIZUNOV

Institute of Mineralogy, Geochemistry  
and Crystal Chemistry of Rare Elements,  
Academy of Sciences USSR, Moscow

## INTRODUCTION

In 1954 during an investigation of the Ege-Khaya tin deposits (Northern Yakutia, Yana-Adychan region) we discovered high indium content in the ore, sometimes reaching tenths of one percent. This suggested an investigation of the distribution of indium in the ores from other Yakutian deposits.

The content of indium was determined in the different ores, minerals, and country rocks from the more interesting tin deposits: Ilintas, Burgochan, Alys-Khaya, Ege-Khaya, Khaton-Khaya, Kester, Deputatsko, Bulatskoe, and Polyarnoe-Omchikandya (Yana-Adychan and Poluosnenskii regions).

In this investigation, special attention was given to the determination of indium in different monomineralic fractions picked under a binocular microscope and checked for purity in thin sections. Spectrography was selected as the basic analytical method.

The results of polarographic analyses made by A. A. Rozbianskaya and of chemical analyses made by L. E. Novorossova are in satisfactory agreement with those obtained by spectrography.

The spectrographic analyses were made by N. V. Lizunov in the spectrographic laboratory of the IMGRE on a quartz spectrograph ISP-22 with three-lens illumination of the slit by the method of three standards. Direct current arc was used.

The weight of each sample was predetermined by a preliminary semi-quantitative analysis, which gave its approximate indium content. The precisely weighed sample (10, 15 or 20 mg, depending on the indium content) was placed in the cavity of the lower electrode or anode of the arc and vaporized. The standards were photographed on every plate. Indium was determined photometrically by measuring the intensity of the indium lines 3039 and 356 Å. With three parallel samples the error in the determination of indium by absolute intensity amounted to  $\pm 10-15\%$ . The limit of detection was 0.001% In.

Of the 2500 quantitative and semi-quantitative indium determinations,

about 500 were made on monomineralic samples.

## A BRIEF GEOLOGICAL DESCRIPTION OF THE DEPOSITS

The investigated tin deposits belong to the following genetic types:

- 1) quartz - cassiterite (greisen) type -- Kester and Polyarnoe-Omchikandya;
- 2) Cassiterite-sulfide -- Deputatskoe, Iintas, Alys-Khaya, Burgochan, Ege-Khaya and Khaton-Khaya;
- 3) polymetallic -- Bulatskoe.

Deposits of the first type are related to the endocontact zones of large biotite granite and alaskite bodies and are of no interest in connection with indium.

The cassiterite-sulfide and polymetallic deposits of the region are genetically related to intrusives of intermediate composition (S. S. Smirnov [7]), ranging from granites to quartz diorites and showing, as a rule, signs of plutonic hybridism (G. L. Padalka [6]). All deposits lie in the monotonous sandstone-shale sequence of the Verkhoyansk-Kolyma complex ( $T_3-J$ ) at various distances from the parent intrusives.

Most of the deposits and the outcrops of the parent intrusives lie in the northwest and northeast trending belts, which, according to Padalka [6] and Smirnov [7], follow the zones of intensive faulting. The deposits were formed at shallow depth. The ore solutions, ascending through the weakened faulted zone, deposited veins mainly of metasomatic type. The process of mineralization consisted of many stages. Almost all cassiterite-sulfide deposits contain ores formed during different stages of the single episode of mineralization (Smirnov [7]). But in the different deposits, depending on the geological structure of the area and the distance from the metallogenic source and other factors, one or another of the stages was manifested with maximum intensity (Table 1)\*.

The mineralogy and geochemistry of the deposits are exceptionally varied and complex. Without enumerating and describing the minerals, we shall mention only that more than 50 elements occur in the various ore bodies and in the enclosing rocks. These elements form about 250 different minerals (the principal ones were described by Smirnov [7]).

## PRINCIPAL MINERALS CONTAINING INDIUM

All minerals which could be separated into monomineralic fractions from all investigated deposits) were analyzed for indium. Indium was found in sphalerite, chalcopyrite, stannite, franckeite, cassiterite, wolframite, and also in arsenopyrite and siderite.

**Sphalerite.** Sphalerite has the highest indium content (Table 2). It is present in all investigated deposits but its amount in the mineral assemblages varies. All sphalerites have high iron content, ranging from 13.1

\*The stages in the formation of the greisen deposits are not discussed, for these deposits are of no interest in connection with indium.



Table 1  
Manifestation of Different Stages of Mineralization in the Cassiterite-Sulfide Deposits of the Region

Deposit	Main stages of mineralization				
	cassiterite-tourmaline (fluorite) * - quartz	cassiterite-chlorite, or tourmaline-quartz with arsenopyrite and iron-rich chlorite	quartz-sulfide, usually with pyrrhotite predominating	sulfide-carbonate, dominant minerals: sphalerite, chalcopyrite, pyrrhotite or pyrite, marcasite, stannite, galena	sulfantimonate-sulfostannate-carbonate
	I	II	III	IV	V
Ilintas	●	Δ	●	Δ	Δ
Alys-Khaya	●	●	Δ	●	—
Burgochan	Δ	●	●	Δ	+
Ege-Khaya	Δ	●	●	Δ	—
Khaton-Khaya	●	Δ	Δ	Δ	+
Deputatskoe	●	●	●	●	●

Symbols: - widely developed, ● - slightly developed, Δ - observed under the microscope only. — absent, + — observed under the microscope only.

\* Typical of the Deputatskoe deposit and to a much less degree, of the Ege-Khaya deposit.

Table 2

## Indium Content in Sphalerite

Type of deposit	Name of deposit	Generation of the mineral	Number of analyzed mono-mineralic samples	Number of samples containing indium	Indium content, %
Cassiterite-quartz (greisen)	Polyarnoe-Omchi-kandya	?	3	3	0.02-0.03
Cassiterite-sulfide	Ege-Khaya	I	25	25	0.005-0.47
		II	5	3	0.001-0.01
		II	2	2	0.01
		II-III	9	8	0.005-0.1
		I	7	7	0.01-0.3
		II	15	15	0.001-0.1
		III	4	3	0.001-0.005
Polymetallic	Bulatskoe	III	15	7	0.001-0.01

to 15.7%. They were formed over a broad interval of time beginning with the earliest substages of the quartz-sulfide stage and ending with the lowest temperature sulfantimonate-sulfostannate stage. Rather tentatively we distinguish three generations of sphalerite, each corresponding to a definite stage of mineralization (III, IV, V, Table 1).

The sphalerite of the first generation was formed during stage III, contemporaneously or nearly so with the first generation pyrrhotite. It has the highest iron content (15.0 - 15.7%) and cryptocrystalline inclusions of pyrrhotite, chalcopyrite, valleriite and chalcopyrrhotite or cubanite.

The second generation sphalerite is usually associated with chalcopyrite or stannite and occurs in carbonate and carbonate-quartz veinlets.

The third generation sphalerite is the latest.

The sphalerites of all three generations were analyzed for indium.

With few exceptions, small amounts of indium were found in all analyzed sphalerites. Its content decreases from the early to the later sphalerites. The maximum indium content (0.47%) was found in a sphalerite of the first generation from the Ege-Khaya deposit. The lowest indium content was found in sphalerite from the Bulatskoe tin-polymetallic deposit.

**Chalcopyrite.** This mineral is rather widely distributed in the sulfide ores (stages II and III), especially in the deposits of the southern group. It is almost always associated with sphalerite and stannite. The early chalcopyrite is associated with sphalerite - I; the latest occurs in the carbonate veinlets. Stannite is the most characteristic member of the chalcopyrite paragenesis.

Indium is very widely distributed in the chalcopyrites (Table 3). The indium content of chalcopyrite rivals that of sphalerite and in some cases

Table 3

## Indium Content in Chalcopyrite

Type of deposit	Name of deposit	Number of analyzed samples	Number of samples containing indium	Indium content, %
Cassiterite-quartz (greisen)	Polyarnoe-Omchi-kandya	2	2	0.005-0.03
Cassiterite-sulfide	Ege-Khaya	9	9	0.005-0.05
	Ilintas	18	18	0.005-0.075
	Alys-Khaya	14	14	0.005-0.03
	Burgochan	2	2	0.01-0.07
	Khaton-Khaya	1	1	0.005
	Deputatskoe	12	12	0.005-0.06

exceeds it. Of the three monomineralic samples of chalcopyrite and three of sphalerite collected in the same areas of the Alys-Khaya deposit, two chalcopyrites had a higher indium content (0.03 - 0.04%) than the sphalerites (0.01%) and one chalcopyrite had the same indium content as the sphalerites. It should be noted also that the indium content is approximately the same in all generations of chalcopyrite.

**Stannite.** The content of the tin sulfide in the ore of the cassiterite-sulfide deposits of Yakutiya usually amounts to tenths of one percent.

Stannite is widely distributed in the Kester greisen deposit, where it forms large segregations in the pegmatites and pneumatolytic-hydrothermal veins.

Chemically, the stannites in all investigated deposits may be divided into zincian (up to 11.16% Zn at Kester) and zinc-free stannites (in all other deposits).

Stannite was formed in the cassiterite-sulfide deposits throughout the entire period of ore deposition at the expense of the earlier cassiterite and independently, during the sulfide phase, together with chalcopyrite and sphalerite. The latest stannite occurs in the Deputatskoe deposit in association with marcasite (replacing pyrrhotite), sphalerite and the carbonates.

Twenty seven monomineralic stannite samples were analyzed for indium (Table 4).

The highest indium content (0.15%) was found in the stannite from the marcasite-stannite-carbonate ores of the Deputatskoe deposit (Table 4 shows that the indium content in stannite from the Deputatskoe and Ilintas cassiterite-sulfide ores is higher than in the stannite of the Kester greisen deposit).

**Franckeite.** Small amounts of indium (0.001 - 0.005%) were found in the latest of the sulfide minerals, franckeite (Deputatskoe deposit). Indium was detected in five out of ten monomineralic samples.

**Cassiterite.** Cassiterite is the principal economic mineral in the ores of the region. Its deposition occurred, with interruptions, throughout the period of mineralization. The main mass of cassiterite was formed during

Table 4

## Indium Content in Stannite

Type of deposit	Name of deposit	Number of analyzed monomineralic samples	Number of samples containing indium	Indium content, %
Cassiterite-quartz (greisen)	Kester	10	8	0.005-0.021
Cassiterite-sulfide	Ilintas	2	2	0.05-0.1
	Deputatskoe	15	15	0.01-0.15

the early stages together with tourmaline, chlorite, and early quartz at the time of deposition of wolframite and arsenopyrite. Quite often cassiterite is associated with pyrrhotite and chalcopyrite, replacing the selvage of the sulfide, and, less frequently, carbonate veins. In some cases it was formed from altered stannite. The segregations of cassiterite are usually very small, ranging from a few tenths to one millimeter in diameter.

The cassiterites from the deposits of the different genetic types have different assemblages of admixed elements. The cassiterites from the deposits formed at the highest temperature (greisen--Omchikandya, Kester) always contain  $Ta_2O_5 + Nb_2O_5$  (tenths of one percent), zirconium (hundredths of one percent) and scandium. The content of scandium in the Omchikandya cassiterite amounts to tenths of one percent. In the cassiterites from the greisen, indium was found in a few samples (in 6 out of 20 samples from Omchikandya and in 2 out of 36 samples from Kester). The indium content in the cassiterites from these deposits does not exceed 0.001% (Table 5).

The cassiterites from the cassiterite-sulfide deposits are characterized by a much lower content of tantalum and niobium oxides (0.002% in the Ilintas and Alys-Khaya deposits and about 0.01% in the Ege-Khaya deposit) and almost always contain indium (Table 5).

This feature had been noted by S. A. Borovik and Ya. D. Gotman [2], L. I. Itsikson and A. K. Rusanov [5], and other investigators in the other provinces of the Soviet Union.

Most commonly, the indium content in cassiterites from the cassiterite-sulfide deposits of Yakutiya amounts to a few thousandths of one percent. Analyses of the earliest and latest cassiterites show that they contain less indium than the cassiterites of the main stages of mineralization. Six monomineralic samples of early cassiterites (from Alys-Khaya, Ilintas and Ege-Khaya) were analyzed. Indium was found in four samples, its maximum content being 0.001%. Of the eight late cassiterites (from Ilintas, Deputatskoe and Ege-Khaya), four contained indium, also in amounts not exceeding 0.001%.

**Wolframite.** This is a fairly common mineral in the tin ores of Yakutiya, but is usually present in small amounts except at the Omchikandya greisen deposit and the Ilintas cassiterite-sulfide deposit. The



Table 5  
Indium Content in Cassiterite

Type of deposit	Name of deposit	Number of analyzed monomineralic samples	Number of samples containing indium	Indium content, %
Cassiterite-quartz (greisen)	Kester	39	2	0.001
	Omchi-kandya (Polyarnoe)	20	6	0.001
Cassiterite-sulfide	Deputatskoe	29	28	0.001-0.01
	Ilintas	23	20	0.001-0.01
	Alys-Khaya	8	4	0.001-0.005
	Ege-Khaya	49	41	0.001-0.01
	Burgochan	8	6	0.001-0.005
	Burgavli	2	2	0.001
	Kirgilyakh	5	3	0.001
	Khaton-Khaya	3	2	0.001

content of iron in wolframite ranges from 17.1 to 20.9% and of manganese from 2.3 to 6.14%.

Approximately 75% of the wolframite samples from the cassiterite-sulfide deposits contain indium (Table 6). The indium content usually amounts to thousandths of one percent (0.001 - 0.005%), the maximum content being 0.01%. No indium was found in wolframite from the Omchi-kandya quartz-greisen deposit.

Indium was found in four samples of arsenopyrite (36 samples were

Table 6  
Indium Content in Wolframite from Cassiterite-Sulfide Deposits

Deposit	Number of analyzed monomineralic samples	Number of samples containing indium	Indium content, %
Ilintas	6	5	0.001-0.01
Alys-Khaya	3	3	0.001-0.005
Deputatskoe	8	5	0.005

alyzed). Its content in arsenopyrite amounts to thousandths of one percent. Traces of indium were detected in two samples of manganosiderite (34 were analyzed).

No indium was found in the other minerals, i.e., in pyrrhotite (55 samples), pyrite (25 samples), marcasite\* (12 samples), galena (13 samples), meneghinite (5 samples), boulangerite (2 samples), tourmaline (23 samples), fluorite (25 samples), topaz (3 samples), bismuthinite (2 samples), and muscovite (12 samples). No indium was found in samples of the shales and sandstones enclosing the deposits, nor in a single one of the analyzed samples of the parent igneous intrusives and dikes.

#### BEHAVIOR OF INDIUM DURING THE FORMATION OF THE CASSITERITE-SULFIDE DEPOSITS OF YAKUTIYA

As has already been pointed out, indium is not characteristic of the reisen deposits. It is widespread in the cassiterite-sulfide deposits and occurs in minerals formed during the different stages of a single episode of re deposition (Table 7), beginning with the earliest and ending with the latest.

Table 7 shows that in the cassiterite-sulfide deposits the third and fourth stages of mineralization, the sulfide-quartz and the sulfide-carbonate stages, are distinguished by the highest indium content.

During the first and second stages, mineralization occurred at rather high temperatures and the principal role in the composition of the ore solutions was played by Si, Al, O, Mg, Fe, B, H, sometimes by F and, in part, by Sn, W, Mn, Cs, Na, K, P, As and S, and among the minor rare elements, by Ti, V, Co, Ta, Nb, Ga, In, Bi, Li, Zr, RE, Y, and Au. Among the principal ore-forming elements of the early stages of ore deposition, indium most closely resembles iron, manganese, and especially tin, both chemically and crystallochemically.

Elements	In <sup>3+</sup>	Sn <sup>4+</sup>	Sn <sup>2+</sup>	Fe <sup>2+</sup>	Mn <sup>2+</sup>
Ionic radii, A	0.92	0.74	1.02	0.83	0.91

Indium and tin have rather similar polarizability, electronegativity, and thermal stability, the properties of their hydroxides and the conditions of formation of sulfides are similar, and they have comparable atomic volumes and almost equal metallic radii. Iron, manganese, and indium are precipitated under very much the same conditions, etc. Therefore, indium accumulates mainly in the minerals containing tin or iron and manganese, i.e., in cassiterite and wolframite and very rarely in arsenopyrite.\*\*

The form in which indium enters into cassiterite and wolframite, minerals with essentially ionic structure, is not definitely known. Vernadskii [1] believed that indium could enter into cassiterite as In<sub>2</sub>O<sub>3</sub> or as some other indium compound not obeying the laws of isomorphism. However, considering the low concentration of indium in the solution, its rather weak

\* Marcasite was formed from pyrrhotite.

\*\* We found no indium in 31 samples of chlorite and other minerals of the first and second stages of mineralization (tourmaline, quartz, etc.).

Table 7

Behavior of Indium During Different Stages of Formation  
of the Cassiterite-Sulfide Deposits

Stage of ore deposition	Principal ore-forming minerals	Maximum indium content, %					
		0.001	0.005	0.01	0.05	0.1	0.5
I Cassiterite-tourmaline (fluorite) - quartz	Fluorite, tourmaline, quartz-I Cassiterite	_____					
II Cassiterite (tourmaline) - chlorite-quartz with arsenopyrite and wolframite	Chlorite, (tourmaline II) quartz-II Cassiterite-II Wolframite Arsenopyrite	_____	_____	_____			
III Sulfide-quartz with predominant pyrrhotite	Quartz, pyrrhotite I, Sphalerite-I Chalcopyrite-I Stannite-I	_____	_____	_____	_____	_____	_____
IV Sulfide-carbonate	Quartz, pyrrhotite-II, pyrite, ankerite, galena, arsenopyrite-II Cassiterite-III Chalcopyrite-II Manganosiderite Sphalerite-II Stannite-II	_____	_____	_____	_____	_____	_____
V Sulfantimonate-sulfostannate-carbonate	Sphalerite-III Franckeite Galena, meneghinite	_____	_____	_____			

affinity for oxygen and its close geochemical resemblance to Sn, Fe, and Mn, it may be suggested, although very tentatively, that in cassiterite  $\text{In}^{3+}$  ions substitute for  $\text{Sn}^{2+}$  ions, which, in the opinion of some crystal chemists (G. B. Bokii) are present in this mineral together with the  $\text{Sn}^{4+}$  ions. In wolframite ( $\text{Mn}^{2+}$ ,  $\text{Fe}^{2+}$ )  $\text{WO}_4$ , indium may with equal ease replace either  $\text{Fe}^{2+}$  or  $\text{Mn}^{2+}$ .

The problem of the charge compensation in cassiterite and wolframite has not been studied at all. It is possible that in wolframite it is accomplished at the expense of niobium, as explained by V. V. Shcherbina, but

the presence of indium in the niobium-poor-wolframites in the cassiterite-sulfide deposits and its "absence" from the niobium-rich wolframites of the Mymchikandya deposit indicates that this hypothesis should be checked on more extensive material.

Superimposed on the earlier "cassiterite" stages, in all investigated deposits, there are later "sulfide" stages (less frequently occurring independently) differing from the earlier sulfide stages in chemical composition and the temperature of the parent solutions (mesothermal). The principal components of these ore-forming solutions were Fe, S, O, Si, Al, H (Ca,  $\text{CO}_2$ ,  $\text{O}_2$  and F in the later stages); the less important components were Sn, Zn, Cu and Ag, Bi, In, Au, Te, Se, Ga, and As; Pb and Tl were present in traces.

Such sulfides as pyrrhotite (pyrite), sphalerite, chalcopyrite, stannite, etc., were deposited from these solutions. Indium was captured by some of these minerals, namely sphalerite, chalcopyrite, and stannite. Inasmuch as sphalerite was regarded until recently as the main carrier of indium, the occurrence of indium in it has been studied rather fully. The problem has been discussed by N. M. Prokopenko, F. E. Abramov and N. K. Rusanov [1]. The mode of occurrence of indium in sphalerite has not been studied experimentally. We shall merely note in this connection that the available data point to the maximum concentration of indium in the sphalerites from the cassiterite-sulfide deposits and cassiterite-polymetallic deposits (the deposits mentioned above and the Pitkaranta, Novonastysrskoe, Bol'shoi Can'on, Lazo's, Aktyuz and others). The indium content in the sphalerites of these deposits often reaches several tenths of the percent. Such high indium content coupled with the irregularity of its distribution in even a single sample of sphalerite, the tendency of indium to form tetrahedral covalent bonds with sulfur and the identical conditions necessary for the formation of zinc and indium sulfides indicate, in our opinion, that besides being present in sphalerite as a diadochic substitute, indium forms independent minerals.

The distribution of indium in chalcopyrite, and especially in stannite, is less well known. In the world literature there are only a few notes on the presence of indium in these minerals--the data by Brewer and Baker [1], Erämetä [10] and Anderson [8]. Our investigations show that indium is very widely distributed in these minerals; moreover, in the content of indium and the frequency of its presence chalcopyrite and stannite from the Kana-Adycha cassiterite-sulfide deposits often do not yield to sphalerite (see chalcopyrite and stannite). It is well known that structurally sphalerite, chalcopyrite, and stannite are very similar; in all of them the basic structure consists of very close packing of sulfur atoms with those of Zn, Cu, or Sn in tetrahedral coordination. The unit cells of chalcopyrite and stannite may be considered as being of the same type as the sphalerite unit cells but double in height and differing from each other merely in the kind of cations occupying the cells. Hence the rather common phenomenon of replacement of one of these minerals by the other effected by regrouping of the cations with the anion structure being preserved (V. V. Ivanov [4]). This, evidently, explains also the presence of indium in these minerals. The presence of rather large amounts of indium in these minerals, the strong affinity of indium for sulfur, and the existence of artificial indium sulfides, some of which have lattice constants very near those of chalcopyrite and stannite (Anderson [8]), suggest that indium sulfide may be present in these minerals in solid solution.\*

A very thorough search failed to discover any independent indium minerals.



As for the other minerals of the sulfide stages (II and IV), we found indium in two specimens of manganosiderite (34 were analyzed). No indium was found in chlorite, pyrrhotite, pyrite, quartz, galena, and other minerals.

In the majority of the deposits of the region, ore deposition virtually ended with the carbonate-sulfide stage. However, at the Deputatskoe deposit, mineralization developed in such a way that during the latest phases of the carbonate-sulfide stage, a specific sulfostannate-sulfoantimonate complex was formed containing franckeite, meneghinite, galena, sphalerite, the carbonates, and locally gypsum. The specific ore-forming elements at this stage were S, Sb, Pb, Sn, Zn, Fe, Ag, Tl, and In. Indium was found in sphalerite and franckeite. It is interesting that in spite of the high iron content in this late sphalerite (13.5%), the indium content is not over 0.005% and averages 0.002%, i.e., a hundred times less than in the early sphalerites (see sphalerite). In franckeite also indium is present in small amounts (not over 0.005%) and was found in only one half of the analyzed samples. No indium was found in meneghinite and galena. The low indium content in the sphalerite and franckeite of this stage of mineralization is due, most likely, to a strong impoverishment of the solutions in indium. In general, a higher indium content may be expected in franckeite. In the franckeite from Santa Cruz (Bolivia), Brewer and Baker [9] found 0.1% In.

### Summary

1. Indium is a typomorphic element of the cassiterite-sulfide deposits of the Yana-Adychansk and Polousnensk regions.
2. Indium is endocryptically captured by the crystal lattices of minerals having mainly ionic bonding, such as cassiterite and wolframite, and by minerals with essentially covalent bonding, such as sphalerite, chalcopyrite, and stannite.
3. The content of indium in the sulfides is usually 10 to 100 times as high as in cassiterite and wolframite, which contain from 0.001 to 0.005%, rarely 0.01% In. In all other analyzed minerals, indium was either not detected at all or was found sporadically and in small amounts, as for example, in franckeite, manganosiderite, and arsenopyrite.
4. The content and frequency of occurrence of indium in chalcopyrite and stannite from the investigated regions are almost always as great as in sphalerites, and sometimes greater.
5. The main mass of indium separated during the second and third stages of the formation of cassiterite-sulfide deposits. During the initial and latest stages of ore deposition, the concentration of indium in the solutions was probably low, for even the mineral-concentrators formed during these stages have rather small indium content.

### REFERENCES

1. Abramov, F.I. and A.K. Rusanov (1939) *Spektroskopicheskoe Issledovanie Tsinkovykh Obmanok na Germanii, Indii, i Gallii* (Spectrographic investigation of sphalerites for germanium, indium, cadmium and gallium). Tr. Vses. n.-i. in-ta mineral'n. syr'ya, vyp. 141.

2. Borovik, S. A. and Ya. D. Gotman (1939). Doklady, vyp. 23, No. 4, Izd. Akad. Nauk SSSR.
3. Vernadskii, V. I. (1911) O Rasprostraneniі Indiya (On the distribution of indium). Izvestiya, 5, No. 3, Izd. Akad. Nauk.
4. Ivanov, V. V. (1958) O Nekotorykh Sluchayakh Unasledovaniya Dvoinikovogo Stroeniya Mineralov (Some cases of inheritance of twinning in minerals). Tr. in-ta min., geokhim. i kristalloghim. redkikh elementov, AN SSSR, vyp. 2.
5. Itsikson, M. I. and A. K. Rusanov (1946). Doklady, vyp. 53, No. 7, Izd. Akad. Nauk SSSR.
6. Padalka, G. L. (1939). Izvestiya, ser. geol., No. 5, Izd. Akad. Nauk SSSR.
7. Smirnov, S. S. et al (1941) Mineralogicheskii Ocherk Yana-Adychanskogo Raiona (Mineralogical essay on the Yana-Adychan region). Tr. In-ta geol nauk AN SSSR, vyp. 46, ser. No. 9.
8. Anderson, J. S. (1953). Geochim. et cosmochim. acta, 4.
9. Brewer, E. and E. Baker (1936). J. Chem. Soc., No. 9.
10. Erametsa, O. (1939) Über die Verbreitung des Indiums in finnischen Mineralen und über seine Trennung von anderen Metallen. Ann. Acad. Sci. Fennicae, Ser. A, 51.

Received for publication  
December 12, 1958.

## DISTRIBUTION OF RARE ALKALIES IN SOIL COLLOIDS AND THE PARTICIPATION OF PLANTS IN THIS PROCESS\*

R. KH. AIDINYAN

V. V. Dokuchaev Soil Institute,  
Academy of Sciences USSR, Moscow

On the basis of the data on the average content of Li, Rb and Cs in the principal types of rocks, recently generalized by A. P. Vinogradov [1], it may be considered as firmly established that the content of these elements in acid rocks is considerably higher than in intermediate and basic rocks. These elements do not form hydrous minerals in the biosphere. Rubidium does not form a single independent mineral. V. I. Vernadskii's observations [2] on the distribution of Rb and Cs led him to the very important conclusion that these elements usually substitute diadochically for potassium and that this is responsible for their relatively high content in potassium aluminosilicates. However, the number of minerals and rocks in which these elements occur in large amounts is very limited. Vernadskii found a relatively high Rb content in some orthoclases (over 1%), and the mazonite from the Il'men' Mountains is especially rich in rubidium (3.12%  $\text{Rb}_2\text{O}$ ). In all the principal potassium-bearing rock-forming minerals--potash feldspars, leucite, micas--Rb accompanies potassium. Goldschmidt [3] came to the same conclusion as Vernadskii. He explained the phenomenon of diadochy by the nearness of the ionic radii of these elements. Using this property of ions, Goldschmidt showed experimentally that clay particles adsorb Rb (and Cs) from aqueous solutions much more strongly than potassium. Later, Noll [4] confirmed theoretically that adsorption depends on the size of the ionic radius and proved that cesium is more strongly adsorbed than rubidium, and the latter, more strongly than potassium. In view of these facts, Goldschmidt admitted the possibility of the accumulation of these elements in argillaceous sediments. Previously, Vernadskii, in discussing the history of rubidium in the earth's crust, reached a broad geochemical generalization concerning the causes of concentration of this element. He was particularly interested in the comparative mobility of rubidium and potassium. The inorganic rubidium salts are no less soluble in water than potassium salts. But, while the potassium content in stream waters is noticeable, that of rubidium is negligible. The concentration of rubidium in the lithosphere is considerably greater than in stream waters. What, then, happens to the concentration of rubidium in the surface

aqueous solutions as they flow towards streams? Rubidium is detained, captured by organisms and soils. Vernadskii ascribed the concentration of b in the weathered mantle not only to inorganic fixation of the element but so to its fixation by living organisms. Bearing this in mind, the present author attempted to determine the distribution of the rare alkalies in the different soil fractions and in the different vegetative organs of plants by making a study of the conjugate system, soil-plants.

Below is a brief description of the method used in this study. The alkalies in the samples were determined spectrographically by the comparison method. The procedure was as follows: the finely powdered samples were introduced into an acetylene flame by means of a blower. The spectra of the standards and of the sample were photographed on the same plate under the same conditions. Quantitative results were obtained by comparing the densities of the lines of a given element in the spectra of the standard and the sample. By using the following lines: lithium--6708 Å, rubidium -- 7800 Å and cesium -- 8521 Å, it was possible to determine the following minimum concentrations: Li --  $1 \cdot 10^{-5}\%$ ; Rb --  $1 \cdot 10^{-4}\%$  and Cs --  $1 \cdot 10^{-4}\%$ . The stability of excitation obtained with acetylene-air flame must be stressed. The order of magnitude of the concentrations of these elements in soils and plants obtained by this method shows that it yields sufficiently accurate and reproducible results. \*

Tables 2 and 3 present some of the averaged data on the content of the rare alkalies in red and yellow soils, chernozems, alluvial-meadow and brown forest soils and in the pre-colloidal and colloidal soil fractions. The content of the rare alkalies in the residues left after the removal of the finely dispersed matter from the soils is also given in the tables. These data show that the total amount of Li, Rb and Cs in the red soils and chernozems is approximately the same as given by A. P. Vinogradov [5] and D. N. Ivanov [6, 7]. The present author's data show that the content of these elements in other soil types differs little from that in the soils listed above. How are the rare alkalies distributed in the different soil fractions and where are they concentrated? This question is quite definitely answered by the data of Tables 1 and 2. It is evident that the colloidal fraction has the highest concentration of the rare alkalies, and the pre-colloidal fraction a lower one. The smaller the diameter of the particles, i. e., the greater the degree of dispersion, the higher is the concentration of these elements. As a rule, the relative content of the rare alkalies in the soil as a whole is much smaller than in its finest fractions. This is especially clearly shown in the cesium and rubidium analyses. While it was possible to detect cesium in the colloidal fractions of many soils by the procedure described above and even to determine its content quantitatively, analyses of the crude samples of the same soils did not reveal the presence of this element. This means that because of the small amount of cesium in the soil it was impossible to detect it without separating the soil into fractions and that cesium is concentrated mainly in the fine fractions. The same is true of rubidium. Tables 1 and 2 show that rubidium and cesium were not detected in the  $100\mu$  fractions of many horizons of different soils, i. e. in the residues left after the colloidal particles had been removed, and this again points to the preferential accumulation of these elements in the soil colloids.

---

The author expresses his gratitude to D. I. Ivanov for valuable advice in spectrographic work.



Table 1  
Lithium, Rubidium and Cesium Content (%) in the Fine Fractions of Red and Yellow Soils and Brown Forest Soils

Soil and its locality	Depth, cm	Lithium				Rubidium				Cesium			
		soil	fraction, $\mu$			soil	fraction, $\mu$			soil	fraction, $\mu$		
			<0.2	0.2-2	2-100 residue		<0.2	0.2-2	2-100 residue		<0.2	0.2-2	2-100 residue
Red soil on striped clay under tea plantation, Makvaneti Kolkhoz, W. Georgia	0-10	3-10 <sup>-3</sup>	15-10 <sup>-3</sup>	10-10 <sup>-3</sup>	1-10 <sup>-3</sup>	10-10 <sup>-3</sup>	30-10 <sup>-3</sup>	20-10 <sup>-3</sup>	1-10 <sup>-3</sup>	0.5-10 <sup>-3</sup>	3-10 <sup>-3</sup>	1-10 <sup>-3</sup>	1-10 <sup>-3</sup>
	20-30	3-10 <sup>-3</sup>	15-10 <sup>-3</sup>	5-10 <sup>-3</sup>	1-10 <sup>-3</sup>	10-10 <sup>-3</sup>	30-10 <sup>-3</sup>	15-10 <sup>-3</sup>	0, 1-10 <sup>-3</sup>	none	1-10 <sup>-3</sup>	0, 1-10 <sup>-3</sup>	none
	36-46	2-10 <sup>-3</sup>	10-10 <sup>-3</sup>	5-10 <sup>-3</sup>	1-10 <sup>-3</sup>	5-10 <sup>-3</sup>	20-10 <sup>-3</sup>	15-10 <sup>-3</sup>	none	»	0.5-10 <sup>-3</sup>	0, 1-10 <sup>-3</sup>	»
	52-62	2-10 <sup>-3</sup>	10-10 <sup>-3</sup>	5-10 <sup>-3</sup>	1-10 <sup>-3</sup>	5-10 <sup>-3</sup>	20-10 <sup>-3</sup>	15-10 <sup>-3</sup>	»	»	0.5-10 <sup>-3</sup>	none	»
	0-10	3-10 <sup>-3</sup>	20-10 <sup>-3</sup>	10-10 <sup>-3</sup>	1-10 <sup>-3</sup>	10-10 <sup>-3</sup>	30-10 <sup>-3</sup>	20-10 <sup>-3</sup>	1-10 <sup>-3</sup>	1-10 <sup>-3</sup>	5-10 <sup>-3</sup>	2-10 <sup>-3</sup>	0, 1-10 <sup>-3</sup>
Yellow soil, slightly podzolized, on shales under tea plantation, Frunze Kolkhoz, Krasnodar region	25-35	2-10 <sup>-3</sup>	20-10 <sup>-3</sup>	5-10 <sup>-3</sup>	0.5-10 <sup>-3</sup>	5-10 <sup>-3</sup>	30-10 <sup>-3</sup>	15-10 <sup>-3</sup>	none	0.5-10 <sup>-3</sup>	5-10 <sup>-3</sup>	1-10 <sup>-3</sup>	none
	50-60	2-10 <sup>-3</sup>	15-10 <sup>-3</sup>	5-10 <sup>-3</sup>	1-10 <sup>-3</sup>	5-10 <sup>-3</sup>	20-10 <sup>-3</sup>	15-10 <sup>-3</sup>	0, 1-10 <sup>-3</sup>	none	2-10 <sup>-3</sup>	1-10 <sup>-3</sup>	»
	80-90	1-10 <sup>-3</sup>	15-10 <sup>-3</sup>	5-10 <sup>-3</sup>	0.5-10 <sup>-3</sup>	1-10 <sup>-3</sup>	20-10 <sup>-3</sup>	15-10 <sup>-3</sup>	none	»	2-10 <sup>-3</sup>	1-10 <sup>-3</sup>	»
	0-15	4-10 <sup>-3</sup>	15-10 <sup>-3</sup>	10-10 <sup>-3</sup>	2-10 <sup>-3</sup>	40-10 <sup>-3</sup>	50-10 <sup>-3</sup>	30-10 <sup>-3</sup>	1-10 <sup>-3</sup>	1-10 <sup>-3</sup>	3-10 <sup>-3</sup>	2-10 <sup>-3</sup>	0, 1-10 <sup>-3</sup>
Brown forest soils on shale under tea plantation, Lenin Kolkhoz, Krasnodar region	20-30	3-10 <sup>-3</sup>	15-10 <sup>-3</sup>	10-10 <sup>-3</sup>	1-10 <sup>-3</sup>	10-10 <sup>-3</sup>	30-10 <sup>-3</sup>	20-10 <sup>-3</sup>	1-10 <sup>-3</sup>	1-10 <sup>-3</sup>	3-10 <sup>-3</sup>	2-10 <sup>-3</sup>	0, 1-10 <sup>-3</sup>
	55-65	2-10 <sup>-3</sup>	10-10 <sup>-3</sup>	5-10 <sup>-3</sup>	1-10 <sup>-3</sup>	5-10 <sup>-3</sup>	30-10 <sup>-3</sup>	20-20 <sup>-3</sup>	none	0.5-10 <sup>-3</sup>	2-10 <sup>-3</sup>	1-10 <sup>-3</sup>	none
	80-90	1-10 <sup>-3</sup>	5-10 <sup>-3</sup>	5-10 <sup>-3</sup>	0.5-10 <sup>-3</sup>	3-10 <sup>-3</sup>	20-10 <sup>-3</sup>	20-10 <sup>-3</sup>	0, 1-10 <sup>-3</sup>	0.5-10 <sup>-3</sup>	2-10 <sup>-3</sup>	1-10 <sup>-3</sup>	»
	100-110	1-10 <sup>-3</sup>	5-10 <sup>-3</sup>	4-10 <sup>-3</sup>	0.5-10 <sup>-3</sup>	3-10 <sup>-3</sup>	20-10 <sup>-3</sup>	20-10 <sup>-3</sup>	none	none	1-10 <sup>-3</sup>	0.5-10 <sup>-3</sup>	»

Note: 3 · 10<sup>-3</sup> represents 3 X 10<sup>-3</sup>.

Table 2  
Lithium, Rubidium and Cesium Content (%) in the Fine Fractions of Chernozems and Alluvial Meadow Soils

Soil and its locality	Depth, cm	Lithium			Rubidium			Cesium			
		soil	fraction, $\mu$		soil	fraction, $\mu$		soil	fraction, $\mu$		
			<0.2	0.2-2		2-100 residue	<0.2		0.2-2	2-100 residue	<0.2
Ordinary chernozem on boulderless structured clay	0-5	2.10 <sup>-3</sup>	10.10 <sup>-3</sup>	5.10 <sup>-3</sup>	0.5.10 <sup>-3</sup>	15.10 <sup>-3</sup>	20.10 <sup>-3</sup>	1.10 <sup>-3</sup>	5.10 <sup>-3</sup>	2.10 <sup>-3</sup>	0.1.10 <sup>-3</sup>
	8-18	2.10 <sup>-3</sup>	10.10 <sup>-3</sup>	3.40 <sup>-3</sup>	1.10 <sup>-3</sup>	15.10 <sup>-3</sup>	30.10 <sup>-3</sup>	20.10 <sup>-3</sup>	3.10 <sup>-3</sup>	1.10 <sup>-3</sup>	none
	45-52	1.10 <sup>-3</sup>	3.40 <sup>-3</sup>	3.40 <sup>-3</sup>	0.5.10 <sup>-3</sup>	10.10 <sup>-3</sup>	30.10 <sup>-3</sup>	15.10 <sup>-3</sup>	0.5.10 <sup>-3</sup>	3.10 <sup>-3</sup>	1.10 <sup>-3</sup>
Chernozem on basalts. Pashiya, area of lake Sevan, Armenian SSR	0-7	3.10 <sup>-3</sup>	5.10 <sup>-3</sup>	4.10 <sup>-3</sup>	1.10 <sup>-3</sup>	20.10 <sup>-3</sup>	30.10 <sup>-3</sup>	0.5.10 <sup>-3</sup>	2.10 <sup>-3</sup>	4.10 <sup>-3</sup>	0.1.10 <sup>-3</sup>
	10-20	2.10 <sup>-3</sup>	5.10 <sup>-3</sup>	3.10 <sup>-3</sup>	4.10 <sup>-3</sup>	20.10 <sup>-3</sup>	40.10 <sup>-3</sup>	30.10 <sup>-3</sup>	1.10 <sup>-3</sup>	4.10 <sup>-3</sup>	3.40 <sup>-3</sup>
	25-30	2.10 <sup>-3</sup>	4.10 <sup>-3</sup>	3.10 <sup>-3</sup>	4.10 <sup>-3</sup>	15.10 <sup>-3</sup>	30.10 <sup>-3</sup>	20.10 <sup>-3</sup>	0.5.10 <sup>-3</sup>	3.10 <sup>-3</sup>	3.10 <sup>-3</sup>
	40-50	2.10 <sup>-3</sup>	4.10 <sup>-3</sup>	3.10 <sup>-3</sup>	1.10 <sup>-3</sup>	10.10 <sup>-3</sup>	30.10 <sup>-3</sup>	20.10 <sup>-3</sup>	0.5.10 <sup>-3</sup>	3.10 <sup>-3</sup>	3.10 <sup>-3</sup>
Alluvial - meadow - steppe soil under tea plantation. Zakataly, Azerbaydzhan SSR	0-10	2.10 <sup>-3</sup>	5.10 <sup>-3</sup>	5.10 <sup>-3</sup>	0.5.10 <sup>-3</sup>	10.10 <sup>-3</sup>	30.10 <sup>-3</sup>	20.10 <sup>-3</sup>	0.5.10 <sup>-3</sup>	2.10 <sup>-3</sup>	1.10 <sup>-3</sup>
	20-30	1.10 <sup>-3</sup>	4.10 <sup>-3</sup>	3.10 <sup>-3</sup>	0.5.10 <sup>-3</sup>	5.10 <sup>-3</sup>	20.10 <sup>-3</sup>	10.10 <sup>-3</sup>	0.1.10 <sup>-3</sup>	2.10 <sup>-3</sup>	1.10 <sup>-3</sup>
	40-45	0.5.10 <sup>-3</sup>	4.10 <sup>-3</sup>	3.10 <sup>-3</sup>	1.10 <sup>-3</sup>	5.10 <sup>-3</sup>	20.10 <sup>-3</sup>	10.10 <sup>-3</sup>	0.5.10 <sup>-3</sup>	2.10 <sup>-3</sup>	0.1.10 <sup>-3</sup>
	60-70	1.10 <sup>-3</sup>	4.10 <sup>-3</sup>	3.10 <sup>-3</sup>	0.5.10 <sup>-3</sup>	5.10 <sup>-3</sup>	20.10 <sup>-3</sup>	10.10 <sup>-3</sup>	0.1.10 <sup>-3</sup>	2.10 <sup>-3</sup>	1.10 <sup>-3</sup>

Note: 2 · 10<sup>-3</sup> represents 2 X 10<sup>-3</sup>.

Lithium is also preferentially concentrated in the colloids, although a considerable amount of it remains in the coarser fractions.

The greater concentration of Li, Rb and Cs in the humic soil horizons as compared with the lower horizons is also noteworthy, and was first pointed out by Vinogradov [5] and later by Ivanov [6]. The same pattern is observed in the distribution of these elements in the fine fractions along the soil profiles (see Tables 1 and 2). It is clear that the colloidal and pre-colloidal fractions of the humus accumulating horizons of these soils almost always contain more Li, Rb, and Cs than the corresponding fractions from the alluvial horizons and from the parent rocks. This fact confirms the existence of the rare alkalis in the form of organic finely dispersed colloidal compounds.

It should be pointed out that in investigations of this kind the method of separation of the colloids is important. The peptizing agents are of little use, since their use requires preliminary treatment of the soil with a base and an acid which remove from it considerable amounts of alkalis. Therefore, to separate the colloids from soils without chemical and thermal treatment, the method of kneading proposed by the author [8] was used. The content of the rare alkalis in the different fractions obtained by this method is near their actual content in these fractions.

What, then, is the form of bonding (besides the already mentioned one) of these elements in the fine soil fractions in which they are concentrated? Several modes of fixation of these elements in the soils and the soil-forming argillaceous rocks are possible. They are different for different fractions. The fractions with particles from 2 to  $0.2\mu$  will not be discussed, for they represent a transitional zone in which most of the primary minerals disappear and secondary minerals are formed. However, some primary minerals (feldspars, hornblende, etc.) often partially preserve their individuality in this zone [9]. We are interested mainly in the forms in which the rare alkalis exist in the fine soil fractions ( $<0.2\mu$ ) composed mainly of the secondary clay minerals. Considering the large surface of these fractions due to the presence of ultra small particles, it may be assumed that cation exchange occurs on the surfaces of the particles determined by the potentials of the ions. Very probable also is adsorption on the inner surfaces of the clay lattices due to the penetration of the ions into the inter-sheet spaces especially in the case of most of the secondary clay minerals which have scaley mica-like structure capable of considerable expansion. Of especial interest are those types of fixation of the rare alkalis which may change from one form to another.

The data of Table 4 show that, after heating, a considerable part of rubidium is not extracted by 0.2N HCl except from the lower horizons of the red and yellow soils. On the other hand, almost all exchangeable rubidium is extracted by the same solvent from unheated colloidal fractions. This means that heating of the soil colloids changes rubidium ions from exchangeable to nonexchangeable form. It is theoretically possible that on being heated the rubidium ion is dehydrated and enters diadochically into the crystal lattices of the clay minerals in soils, i.e., becomes nonexchangeable. A certain confirmation of this type of adsorption in the case of lithium is found in the works of Greene-Kelly [10]. He showed that lithium saturated montmorillonite dehydrates on heating, its interplanar spacings diminish sharply and a part of lithium becomes nonexchangeable. Still earlier, Hofmann and Klemen [11] came to the conclusion that the decrease in the capacity of Li-montmorillonite lattice to expand after drying is related to the migration of Li ions from the interlayer positions into the open

The Effect of Temperature on the Mobility of Rubidium in Soil Colloids ( $<0.2\mu$  fraction). Rb in %

Soil	Sampling depth, cm	Before heating		After treatment with 0.2N HCl		After heating at 170°C followed by treatment with HCl	
		initial amount	Rb enrichment	initial amount	Rb enrichment	initial amount	Rb enrichment
Red	0-10	$30 \cdot 10^{-3}$	$10 \cdot 10^{-2}$	$25 \cdot 10^{-3}$	$25 \cdot 10^{-3}$	$30 \cdot 10^{-3}$	$7 \cdot 10^{-2}$
	52-62	$20 \cdot 10^{-3}$	$7 \cdot 10^{-2}$	$15 \cdot 10^{-3}$	$15 \cdot 10^{-3}$	$15 \cdot 10^{-3}$	$15 \cdot 10^{-3}$
Yellow	0-10	$20 \cdot 10^{-3}$	$10 \cdot 10^{-2}$	$15 \cdot 10^{-3}$	$15 \cdot 10^{-3}$	$20 \cdot 10^{-3}$	$7 \cdot 10^{-2}$
	50-60	$15 \cdot 10^{-3}$	$10 \cdot 10^{-2}$	$10 \cdot 10^{-3}$	$10 \cdot 10^{-3}$	$10 \cdot 10^{-3}$	$10 \cdot 10^{-3}$
Brown forest soils	0-10	$30 \cdot 10^{-3}$	$7 \cdot 10^{-2}$	$20 \cdot 10^{-3}$	$20 \cdot 10^{-3}$	$30 \cdot 10^{-3}$	$5 \cdot 10^{-2}$
Common	55-65	$20 \cdot 10^{-3}$	$10 \cdot 10^{-2}$	$15 \cdot 10^{-3}$	$15 \cdot 10^{-3}$	$20 \cdot 10^{-3}$	$7 \cdot 10^{-2}$
	0-10	$50 \cdot 10^{-3}$	$25 \cdot 10^{-2}$	$40 \cdot 10^{-3}$	$40 \cdot 10^{-3}$	$50 \cdot 10^{-3}$	$20 \cdot 10^{-2}$
chernozem	42-52	$30 \cdot 10^{-3}$	$10 \cdot 10^{-2}$	$20 \cdot 10^{-3}$	$20 \cdot 10^{-3}$	$30 \cdot 10^{-3}$	$7 \cdot 10^{-2}$

Note. The colloids were enriched in Rb by washing in 0.01 N solution of RbCl in a Gooch crucible with applied suction. Each sample was treated 10 - 12 times with small portions of solution and the excess of salt was rinsed out with distilled water until disappearance of reaction for Cl. Thus, the samples were enriched with exchangeable (mobile) rubidium to a different degree. Rubidium was extracted with 0.2 N solution of HCl. Each gram of colloidal material was treated with 50 mg of solution applied in portions. The colloids were dried in the crucibles and the remaining rubidium was determined. The amount of exchangeable (mobile) rubidium was estimated by the content of the element before and after HCl treatment. The colloids were heated at 170°C for 40 hours. During heating the colloids were moistened several times.

$30 \cdot 10^{-3}$  represents  $30 \times 10^{-3}$ .



octahedral positions. Evidently rubidium is not the only cation which becomes strongly bonded in soils after dehydration. The behavior of rubidium in adsorption is in many ways similar to that of potassium. Potassium also changes to nonexchangeable form as the result of heating. This fact was established long ago for soils and different sorbents [12, 13, 14, 16]. It should be noted that, like potassium, rubidium is more strongly adsorbed by heating on the chernozems than on the red and yellow soils. Evidently the lyophilic organic and organic-mineral colloids of the chernozems bond rubidium more securely in drying than colloids composed mainly of the sesquioxides.

The red and yellow soils exhibit a dual nature so far as the fixation of rubidium by dehydration is concerned. Rubidium becomes bonded in the upper accumulative humic horizons after thermal treatment, but not in the deeper horizons.

These phenomena are important biogeochemically in connection with the migration of the rare alkalis in the system: weathered mantle-soil-plants.

Inasmuch as desiccation of soils diminishes the amount of mobile elements by nonexchangeable adsorption, their concentration in soil solutions also is diminished. Under natural conditions this may affect the availability

Table 4

Lithium, Rubidium, Cesium and Potassium Content  
in the Different Vegetative  
and Reproductive Organs of the Tea Plant

Parts of the tea plant	% in ash			
	lithium	rubidium	cesium	potassium
First leaf and bud	$1 \cdot 10^{-3}$	$40 \cdot 10^{-3}$	$1 \cdot 10^{-3}$	41,2
Second leaf	$1 \cdot 10^{-3}$	$25 \cdot 10^{-3}$	$0,5 \cdot 10^{-3}$	40,3
Third leaf	$1 \cdot 10^{-3}$	$20 \cdot 10^{-3}$	$0,5 \cdot 10^{-3}$	38,7
Flesh (productive shoot with 3 leaves and a bud)	$1 \cdot 10^{-3}$	$25 \cdot 10^{-3}$	$0,5 \cdot 10^{-3}$	39,2
Coarse old leaves	$0,5 \cdot 10^{-3}$	$5 \cdot 10^{-3}$	none	25,4
Fruits	$0,5 \cdot 10^{-3}$	$10 \cdot 10^{-3}$	»	31,7
Flowers	$1 \cdot 10^{-3}$	$25 \cdot 10^{-3}$	$0,5 \cdot 10^{-3}$	38,9
Year-old stems	$0,5 \cdot 10^{-3}$	$5 \cdot 10^{-3}$	none	30,2
Stems many years old	none	$0,5 \cdot 10^{-3}$	»	21,3
Central roots	»	$0,5 \cdot 10^{-3}$	»	23,4
Side roots	»	$0,5 \cdot 10^{-3}$	»	22,1
Small roots	»	$0,5 \cdot 10^{-3}$	»	21,5

Note: Comma represents decimal point.

of the rare alkali compounds to plants.

Certain conclusions about the mobility of the rare alkalies after treatment with 0.2N HCl and hence, about their availability to plants, may be drawn from Table 3.

Evidently the mobility of the rare alkalies varies within rather broad limits. From 10 to 30% of the total content of the rare alkalies may be mobile. This means that in the soils a considerable part of the rare alkalies exists in a form available to plants.

What is the effect of the condition of the soil on the absorption of the rare alkalies by plants? This effect is best determined by a combined analysis of soil and of the plants growing on it. A more correct idea is gained in this way of the magnitude and intensity of absorption of the rare alkalies by plants than is given by separate analyses.

Table 4 gives the content of Li, Rb and Cs in different vegetative and reproductive organs of the tea bush. These are average figures for plants growing on acid yellow soils. Approximately the same data were obtained for Li, Rb and Cs for tea plants growing on red soils. No cesium was found in the leaves of tea bushes growing on red soils, although the content of this element in the yellow and red soils is the same (Table 4).

It follows from the data of Table 4 that tender tea leaves contain more rubidium than do old, coarse leaves. The flowers and fruit of the tea bush are also somewhat enriched in rubidium. This pattern of distribution of rubidium holds for all tea plants growing on different soils in the main tea-growing regions of the USSR. It does not hold for the distribution of lithium and in part of cesium in the vegetative organs of the tea bush, although these elements do show a tendency to accumulate in the younger organs. The amount of rubidium in tea plants, especially in the leaves of different age, increases with increase in their potassium content (Table 4), although this correlation is not linear. A confirmation of this is found in analyses of other plants (Tables 7 and 8). It is very probable that in plants rubidium may play the same physiological role as potassium, which is the most important element in plant nourishment.

Like potassium, rubidium is easily extracted from plants by water, and this indicates that it is present in plants mainly as ions or in an easily soluble form. Considerably more than half the total rare alkalies is extracted from a sample of tea plant (ground up in a mortar) when the ratio of plant to hot water is 1 to 100 (with one 30-minute stirring) (Table 5).

The data of Table 5 on the extraction of the rare alkalies from the same parts of a plant by means of electrodialysis is of considerable interest. The amount of the rare alkalies extracted by electrodialysis is greater than the amount determined in the ash (the initial amount was determined in the ash and recalculated to the plant). This is not a contradiction. It may be said quite definitely that when plants are reduced to ash a certain amount of the alkalies is volatilized. \* Cesium volatilizes especially easily. The determination of the rare alkalies made on electrodialytically separated ions are more accurate. Spectrography failed to detect cesium in two ash samples, but it was found in the electrodialytic extract from the same samples (Table 5).

---

\* The volatilization of the rare alkalies during reduction to ash may be decreased by doing this at the lowest possible temperature (not over 400°C).

Table 5

Extraction of Li, Rb and Cs from the Vegetative Organs  
of the Tea Bush by Water and by Electrodialysis.  
In mg per 100g of Plant Matter

Parts of the tea plant	Lithium			Rubidium			Cesium		
	initial amount	extracted		initial amount	extracted		initial amount	extracted	
		water	electro- dialysis		water	electro- dialysis		water	electro- dialysis
Flesh	0.5	0.4	0.6	5	4	6	1	0.6	2
Coarse leaves	0.5	0.4	0.5	3	2.5	4	not de- tected	0.5	0.5
Stems	0.2	0.1	n. d.	0.2	n. d.	0.5	"	none	none
Roots	0.2	0.1	0.4	0.2	0.1	0.5	"	"	0.5

Note. Electrodialysis was performed in the Pauli three-chamber apparatus at 20v/cm. Each sample was electrodialyzed for 48 hours.

To what extent are Li and Rb extracted from the leaves of oak, maple and birch under natural conditions? A few data on the content of these elements in fresh and old fallen leaves are presented in Table 6. A comparison of these figures shows that Li and Rb are rapidly extracted from old fallen leaves which have lain on the ground less than a year. This is the reason why the two elements were not found in the old birch leaves and Li, in old maple leaves. The same table shows that Li and Rb are energetically leached out of the forest duff, for here the content of these elements is about the same as in old fallen leaves.

The data on the accumulation and leaching of the rare alkalies in the steppe vegetation growing on the same chernozem soils are equally convincing. Tables 7 and 8 give the content of these elements in the living and dead stems and leaves of the principal steppe and steppe-meadow plants. Calamagrostis epigeios, Stipa joannis and Festuca sulcata, and in their roots in different soil horizons. It follows from these data that the rare alkalies have the same distribution in these plants as in other analyzed plants growing on different soils.

Comparing the amount of the rare alkalies in the living stems and leaves of Calamagrostis epigeios, Stipa joannis and Festuca sulcata with the amount in the plant debris (under natural conditions) subjected to atmospheric effects for a year, the rate of their migration from the debris into the soil may be estimated (Table 7). Evidently removal of these elements from the stems and leaves occurs during the life of the plant, but it is greatly accelerated after death by inorganic and organic processes.

Cesium was not found in the debris composed of different types of plants. It is absent also from the living stems and leaves of Festuca sulcata (Table 7). But, as Table 8 shows, cesium is present in both living and, what is

Table 6

Li, Rb and Cs Content in Fallen Leaves and in the Forest Litter  
of the Kamennaya Steppe

Determined on:	% in ash		
	lithium	rubidium	cesium
Leaves of oak			
fresh fall	$1,5 \cdot 10^{-3}$	$30 \cdot 10^{-3}$	none
old fall	$0,5 \cdot 10^{-3}$	$10 \cdot 10^{-3}$	»
Leaves of birch			
fresh fall	$1 \cdot 10^{-3}$	$15 \cdot 10^{-3}$	»
old fall	none	none	»
Leaves of maple			
fresh fall	$0,5 \cdot 10^{-3}$	$30 \cdot 10^{-3}$	$0,5 \cdot 10^{-3}$
old fall	none	$5 \cdot 10^{-3}$	none
Forest floor (oak and birch section)	$0,1 \cdot 10^{-3}$	$5 \cdot 10^{-3}$	»

Note: Comma represents decimal point.

Especially interesting, dead roots in the different soil horizons. Lithium and rubidium are invariably present in living and dead roots in various soil horizons. It should be noted that the content of Rb (Cs) and possibly of Li in the living roots tends to increase downwards in the soil profile. Evidently this is related to the size and age of the roots, for only small and tender roots penetrate to the depth of 40-50 cm (horizon B<sub>1</sub>), especially since in the unmowed areas of the steppe where sampling was done, there were about 160 associations with different degrees of development of the root system. The amount of roots in the upper horizons of the chernozem down to the depth of 18 cm is approximately 170 metric centners per hectare, while in the lower horizons (50-50 cm) it does not exceed 9 centners/ha. Taking the weight of the roots and of their ash into account, and using the data of Table 8, it was possible to calculate the amount of Li, Rb and Cs in the living and dead roots in each of the chernozem horizons of the unmowed part of the Kamennaya steppe (Voronezh district). These data are given in Table 9.

Table 9 shows that the total amount of rare alkalies in living and dead roots decreases sharply down the soil profile with diminution of root mass. The amount of Li in roots of the cultivable layer does not exceed 45 g/ha, that of Rb is about 200 g/ha and the Cs content is not more than 7 g/ha. The total weight of the stems and leaves of the meadow-steppe vegetation is



Table 7

Li, Rb, Cs and K Content in the Grasses  
of the Kamennaya Steppe

Plant	% in ash			
	lithium	rubidium	cesium	potas- sium
<u>Calamagrostis</u> <u>epigeios</u> above ground	$2 \cdot 10^{-3}$	$50 \cdot 10^{-3}$	$0,5 \cdot 10^{-3}$	12,31
debris	$0,1 \cdot 10^{-3}$	$0,1 \cdot 10^{-3}$	none	0,88
<u>Stipa joannis</u> above ground	$3 \cdot 10^{-3}$	$30 \cdot 10^{-3}$	$0,5 \cdot 10^{-3}$	10,13
debris	$0,5 \cdot 10^{-3}$	$0,1 \cdot 10^{-3}$	none	1,20
<u>Festuca sulcata</u> above ground	$2 \cdot 10^{-3}$	$25 \cdot 10^{-3}$	»	8,10
debris	$0,5 \cdot 10^{-3}$	$0,5 \cdot 10^{-3}$	»	0,72

Table 8

Li, Rb, Cs and K Content in the Root Mass  
in the Different Horizons of Chernozem  
on Unmown Steppe

Soil horizon and depth of sampling of the root mass, cm	% in ash			
	lithium	rubidium	cesium	potas- sium
A <sub>1</sub> 0—8				
live	$5 \cdot 10^{-3}$	$30 \cdot 10^{-3}$	$1 \cdot 10^{-3}$	4,28
dead	$3 \cdot 10^{-3}$	$10 \cdot 10^{-3}$	$0,5 \cdot 10^{-3}$	1,56
A <sub>2</sub> 8—18				
live	$10 \cdot 10^{-3}$	$50 \cdot 10^{-3}$	$1,5 \cdot 10^{-3}$	6,33
dead	$3 \cdot 10^{-3}$	$5 \cdot 10^{-3}$	$0,5 \cdot 10^{-3}$	1,74
B <sub>1</sub> 40—50				
live	$10 \cdot 10^{-3}$	$70 \cdot 10^{-3}$	$2 \cdot 10^{-3}$	6,80
dead	$2 \cdot 10^{-3}$	$15 \cdot 10^{-3}$	$0,5 \cdot 10^{-3}$	1,65

Note: Comma represents decimal point.

Table 9

Total Li, Rb and Cs in the Plant Roots  
in Different Soil Horizons

Roots	Horizon and depth of sampling, cm	Weight of root ash, kg/ha	Grams per hectare		
			lithium	rubidium	cesium
Live	A <sub>1</sub> 0—8	474	23	142	4
	A <sub>2</sub> 8—18	120	4	12	0,6
	B <sub>1</sub> 40—50	38,5	4	27	0,8
Dead	A <sub>1</sub> 0—8	398,5	12	40	2
	A <sub>2</sub> 8—18	95	2,8	4,7	0,5
	B <sub>1</sub> 40—50	8,8	0,2	1,3	0,04

Note: Comma represents decimal point.

from 1/2 to 1/3 of the weight of the roots. The main role in the biological accumulation of the rare alkalies in the chernozem horizons under meadow-steppe vegetation is played by the root mass.

The majority of steppe and meadow-steppe vegetation is perennial, and therefore only part of the root mass, namely the dead roots, are subjected to yearly decay, leaching and mineralization. The amount of rare alkalies and other elements [15] annually delivered to the soil by the root mass may be approximately estimated from the mass of the dead roots. The mass of the dead roots is considerable and only a little less than that of the living roots. As is to be expected, the living roots contain a little more of the rare alkalies than the dead roots, but they yield them to the soil less intensively than do the parts of the plants exposed above the surface. Whatever the source of accumulation of these elements in the soil, the root systems pump Li, Rb and Cs out from the deeper soil horizons and enrich the upper humic horizons in these mobile elements. The rare alkalies, made mobile by the mineralization of the dead roots and the leaching of the stems and leaves on the surface of the soil, are adsorbed on the finely dispersed particles. Thus the soil colloids become enriched in these elements.

### Summary

Soils and the plants growing on them were analyzed for rare alkali content.

It was established experimentally for the different types of soils that the largest amount of the rare alkalies accumulates in the colloids ( $<0.2\mu$  fraction), and a smaller amount in the pre-colloidal fraction ( $2 - 0.2\mu$ ) of the soils. In many cases no rubidium or cesium was found in the residue

left after the separation of particles  $<2\mu$  in diameter. While it was possible to determine cesium quantitatively in the colloids, very often no cesium was detected in crude samples of the same soil. The relative content of the rare alkalies in the soil as a whole is very much smaller than in its fine fractions. As a rule, the smaller the diameter of the particles, i.e., the greater the degree of dispersion, the greater the accumulation of the rare alkalies. It is suggested that adsorption of the rare alkalies on the inner surface of the colloidal particles in the interlayer spaces is one of the forms of fixation of the rare alkalies in soils. It has been shown that heating of the soil colloids changes rubidium from exchangeable to non-exchangeable form, evidently because the dehydrated ion enters into the open octahedral spaces of the crystal lattices. Exceptions to this are colloids containing large amounts of the sesquioxides (colloids separated from the lower horizons of red and yellow soils).

A considerable portion of the rare alkalies, amounting to 10-30% of the total content, exists in a mobile form (soluble in 0.2N HCl).

The rubidium content in plants (in tea leaves, steppe vegetation, etc.) is correlatable with their potassium content. Like potassium, rubidium accumulates in the tender vegetative and reproductive organs of the plants. It is possible that in plants rubidium may substitute for potassium. The "flesh" of a tea plant always contains more rubidium and cesium than the coarse leaves. No cesium was found in the ash of old leaves, flowers and roots of the tea plant. Under natural conditions, under the effect of atmospheric agents and geological processes, lithium, rubidium and cesium are intensively leached out of dead leaves on the forest floor, and out of dead roots, so that the soil is enriched in these elements, especially its humic horizon. During the formation of soil, this process gives an increased content of the rare alkalies to the soil colloids.

#### REFERENCES

1. Vinogradov, A. P. (1956). *Geokhimiya*, No. 1.
2. Vernadskii, V. I. (1954) *Izbrannye Sochineniya*, t. I (Selected Works, v. I). Izd. Akad. Nauk SSSR, Moscow.
3. Goldschmidt, V. M. (1938) *Sbornik Statei po Geokhimii Redkikh Elementov* (Collection of papers on the geochemistry of rare elements)... Moscow-Leningrad.
4. Noll, W. (1931) *Über die geochemische Rolle der Sorption*. *Chemie der Erde*, 6, p. 552.
5. Vinogradov, A. P. (1957) *Geokhimiya Redkikh i Rasseyannykh Khimicheskikh Elementov v Pochvakh* (Geochemistry of rare and dispersed elements in soils). Izd. Akad. Nauk SSSR.
6. Ivanov, D. N. (1954). *Pochvovedenie* (Soil science), No. 2.
7. Ivanov, D. N. (1956) *Rasprostranenie Litiya, Rubidiya i Tseziya v Productakh Sovremennogo Vyvetrivanija i v Pochvakh* (Distribution of lithium, rubidium and cesium in the modern products of weathering and in soils). Collection: *Weathered mantle*, vyp. 2. Izd. Akad. Nauk SSSR.
8. Aidinyan, R. Kh. (1947). *Kolloidn. zh.*, t. IX, No. 1.
9. Aidinyan, R. Kh. (1952). *Doklady*, 83, No. 2, Izd. Akad. Nauk SSSR.
10. Greene-Kelly, R. (1955) *Dehydration of the montmorillonite minerals*. *Mineralogical Magazine*, XXX, No. 228.

- . Hoffmann and Klemen (1955) Verlust der Austauschfähigkeit von Lithiumionen an Bentonit durch Erhitzung. Zeits. Anorg. Chem., 262.
- . Grobunov, N. I. (1936) Vysushivanie Pochvy i Neobratimoe Pogloshchenie Kaliya (Drying of soil and permanent adsorption of potassium). Tr. konf. molodykh uchenykh VIUAA.
- . Hangland and Martin (1933) Adsorption of potassium by plants in relation to replaceable, nonreplaceable, and soil solution of potassium. Soil Science, 36, No. 1.
- . Volk, N. J. (1934) The fixation of potassium in difficultly available form in soils. Soil Sci., 37, No. 4.
- . Aidinyan, R. Kh. (1954). Pochvovedenie, No. 1.
- . Antipov-Karataev, I. N., S. I. Ponomareva and P. V. Astaf'ev (1935) Ob Adsorptsii Kaliya i Fosfat-Ionov Pochvami (On adsorption of potassium and phosphate ion by soils). Tr. Loviua, vyp. 36.

Received for publication  
May 20, 1958.



## URANIUM AND THORIUM IN THE INTRUSIVE ROCKS OF CENTRAL AND WESTERN TUVA

I. I. ABRAMOVICH

All-Union Geological Research Institute, Leningrad

The present paper is based on the material collected by the author during the period 1955-1957 and is intended to provide basic information on the average uranium and thorium content in the intrusive rocks of Central and Western Tuva, no studies of radioactive elements having been made in these territories heretofore.

Intrusive igneous rocks are an important feature of the geology of Tuva. They form many complexes differing in age and composition. Of the many schemes of classification of these complexes proposed at different times [1, 2], the best documented is the one proposed by T. N. Ivanova, based on numerous absolute age determinations by the potassium-argon method [3]. The basis of Ivanov's scheme is the concept of two geosynclinal cycles in the development of the Central Tuva depression. The second cycle produced structures resembling V. A. Nikolaev's [4] geosynclines of the second order. A magmatic cycle is associated with each of the geosynclinal cycles and includes intrusives corresponding in character to the initial, early, middle and later stages of the development of mobile zones as conceived by Yu. A. Bilibin [5].

The beginning of the first, Lower Paleozoic cycle was marked by the intrusion of ultrabasic rocks of the Aktovrak complex, whose age may be given with considerable certainty as Lower Middle Cambrian. The multiphase Tannu-ola complex, mainly diorite-plagiogranite in composition, is widely exposed in the East Tannu-ola Range and is evidently Upper Cambrian, or at least pre-Ordovician. Somewhat younger are the pre-Silurian batholithic, essentially granitic masses of the Chingegat complex (Chingegat, Monguntaiga, Tungul' and other massifs).

The Middle Paleozoic magmatic cycle is represented by many relatively small intrusions (a few tenths of a kilometer to a few kilometers in diameter), of varied composition, often dike-like, and sometimes of clearcut hypabyssal aspect. Among these intrusives are pyroxenites of the Akkhem complex marking the beginning of the cycle; the mainly basic dikes and sills comagmatic with the Lower Devonian extrusives; the granites of the Khovaksy complex, the potassic granites of the Syutkhol' complex carrying rare metals, the granite porphyries and felsite porphyries comagmatic with

Intrusive cycles	Name of complex	Age	Dominant rocks	Results of tests				
				luminescence analysis		radiochemical analysis		
				No. of samples	U · 10 <sup>-4</sup> %	No. of samples	U · 10 <sup>-4</sup> %	Th · 10 <sup>-4</sup> %
Lower Paleozoic	Aktovrak Tannu-ola	Cm <sub>1</sub> -Cm <sub>2</sub> Cm <sub>2</sub> -Cm <sub>3</sub>	Ultrabasic Gabbros Diorites Tonalites, granites Granites	6	<1.0	1	<0.9	< 3
				10	<1.0	3	<0.9	3
				45	1.2	8	1.4	7
	Chingekat	Cm <sub>3</sub> -O <sub>1</sub>	Pyroxenites, Serpentinities Diabase porphyries	64	2.6	12	2.5	13
				56	3.3	12	4.0	24
								5 6
Middle Paleozoic	Akkhem  Intrusives comagmatic with Lower Devonian effusives Khovaksin Syutkhol  Intrusives comagmatic with Middle Devonian effusives Torgalyk	up to D <sub>1</sub>  D <sub>1</sub>		13	<1.0	2	0.9	< 3
				20	1.8	2	1.5	6
		D <sub>1</sub> -D <sub>2</sub> up to D <sub>2</sub> <sup>2</sup>	Granites Microcline granites Felsite- porphyries, quartz- feldspar	13	2.1	4	2.1	5
				96	4.0	21	4.5	15
		D <sub>2</sub>	porphyries Gabbro- diorites Granites, syenites	30	2.7	5	2.8	13
				33	1.5	4	1.2	4
		D <sub>2</sub> -D <sub>3</sub>		41	3.0	10	3.2	13
								4.1
		D <sub>3</sub> -C <sub>1</sub>	Granites	24	8.7	6	8.1	36
								4.5



the Middle Devonian extrusives, and the rocks of the latter part of the cycle, the gabbroids and their acid and alkalic differentiates of the Torgalyk complex. A special position is occupied by the post-Upper Devonian granites of the Yustyd complex exposed only in the extreme southwest in the Chikhachev range. A list of the complexes, with their age sequence, is given in the table.

The method of obtaining the average content of the radioactive elements in the intrusives was briefly this: The average content of uranium and thorium was determined by luminescence and radiochemical analyses of samples of fresh rocks collected mainly from outcrops. Each analyzed sample was a mixture of several samples weighing 100-200 mg, powdered and split in the usual manner. For control and additional radiochemical determinations of thorium, numerous averaged results of the gamma-activity measurements of the rocks were used. Data obtained from well exposed bedrock by air-borne surveys were also widely used. The potassium content of the rocks was not determined, because the rather numerous published chemical analyses of the Tuvan rocks sufficed to estimate the average percentage of this element in almost every one of the massifs with sufficient accuracy for the required calculations.

The average uranium and thorium content in each of the sixty sampled massifs is presented in Fig. 1. The principle of construction of the diagram needs no explanation. Examination of the diagram shows, first of all, that the intrusives of similar composition and age belonging to the same intrusive complex are characterized by very similar or equal content and ratio of the radioactive elements. This feature in the behavior of uranium and thorium was long ago noticed by a number of investigators, and is well illustrated in the work of L. V. Komlev. The constancy of the thorium-uranium ratio in the genetically related intrusives is consonant with the principle of para-elements [6, 8 etc.] and is due to the common geochemical history of the radioactive elements during intrusive magmatism. In



addition to the results of sampling of massifs whose age and membership in a given complex is firmly established ("standard massifs"), Fig. 1 includes data for some massifs whose ages are not definitely known and concerning which most contradictory opinions are entertained by the geologists of Tuva. Such, for example, are the Kyzyl'dag, Shugur, Chinge, Tongul' and some other massifs. The radiochemical characteristics obtained for them may be considered as additional objective criteria of the correctness of referring these massifs to the Syutkhol', Torgalyk and Chingekat complexes, especially as this does not contradict the geological data.

The dependence of the average uranium content on the petrography of the rock is especially clearly shown by the intrusives of the Tannu-ola complex, whose composition varies regularly from gabbro and gabbro-diorite to biotite granites and alaskites. The diagram of Fig. 2 shows that the thorium and uranium content increases uniformly from the basic to the acid rocks. An analogous picture is presented by the intrusives of the Torgalyk complex. Thus the clearcut dependence of the uranium-radium content on the basicity of the rocks, first shown by Strutt and repeatedly confirmed by

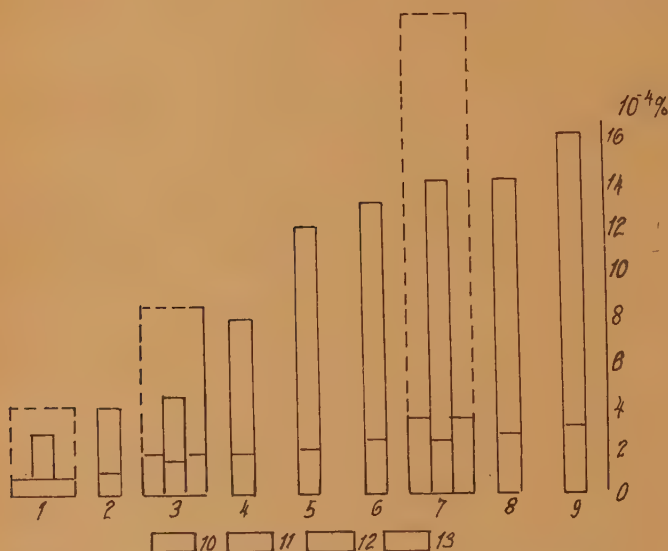


Fig. 2. Uranium and thorium content in the rocks of the Tannu-ola complex

1 -- gabbro, 2 -- gabbro-diorite, 3 -- diorite, 4 -- quartz diorite, 5 -- plagiogranite and adamellite, 6 -- hornblende granite, 7 -- biotite and two-mica granite, 8 -- granodiorite (endocontact variety of biotite granite), 9 -- alaskite, 10 -- uranium content, 11 -- thorium content, 12 -- average uranium content in basic, intermediate and acid rocks respectively, according to A. P. Vinogradov, 1956, 13 -- the same for thorium

later investigations [10, 11], is confirmed once more by the analysis of the Tuvan material.

Having data on the radiochemical characteristics of the individual intrusive complexes (Table), it is possible to trace the principal regularities in the variation of the content of radioactive elements in the intrusive igneous rocks as a function of their age, i. e., to trace the geochemical history of uranium and thorium during the evolution of intrusive magmatism of a given region. The diagram of Fig. 3 shows the regular cyclic character of the behavior of radioactive elements in time. The first, the earliest geochemical cycle of uranium and thorium, corresponds to the intrusive cycle of the

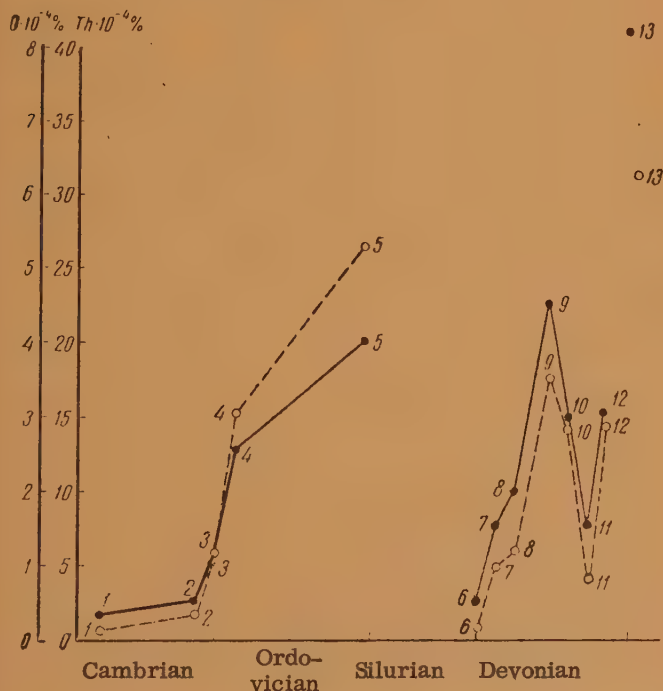


Fig. 3. Uranium and thorium in the evolution of intrusive magmatism in Central and Western Tuva

1 -- Aktovrak complex, 2 -- rocks of the first phase of the Tonnu-ola complex, 3 -- same, second phase, 4 -- same, third phase, 5 -- Chingekat complex, 6 -- Akkhem complex, 7 -- rocks comagmatic with the Lower Devonian effusives, 8 -- Khovaksy complex, 9 -- Syutkhoh complex, 10 -- rocks comagmatic with the Middle Devonian effusives, 11 -- gabbroids of the Torgal' complex, 12 -- granitoids, 13 Yustyd complex, solid lines -- uranium, interrupted lines -- thorium

Lower Paleozoic geosyncline of Tuva; the second, to the intrusive cycle of Nikolaev's second order geosyncline. The principal difference between the cycles consists mainly in this: the role of uranium in the younger cycle is relatively greater than in the older. Moreover, the general duration of the second cycle was at least two or three times as short as that of the first and covered only one period (Devonian). To the believers in a single magmatic cycle in the region the last circumstance served as proof of the incorrectness of separation of a second cycle. It may be noted in this connection that the platform magmatic cycles are usually even shorter, and often fall into an interval of time corresponding to a single age [9]. The time of their manifestation corresponds to the moment of the most intensive tectonic phase in the neighboring geosyncline. As for the regions of transitional type, such as Nikolaev's second order geosynclines, it is quite understandable that their magmatic cycles must be longer than the platform cycles but considerably shorter than the typical geosynclinal magmatic cycles.

Some time ago, L. V. Komlev, in summarizing the many years' work on the average uranium and thorium content in the granitic massifs of the Soviet Union, separated five main types of granitic massifs. If the existence of massifs of the transitional type mentioned by Komlev [7] is neglected, the characteristics of each of the main radiochemical types may be shown graphically, as was done earlier. Then the position of the Tuvan granitoids among Komlev's generalized radiochemical types can be determined. An examination of Fig. 4, which illustrates this, leads to the following conclusions.

1. The granitoids of the Tannu-ola complex most closely resemble the granitoids of type V but differ from them in having a somewhat higher Th/U ratio.

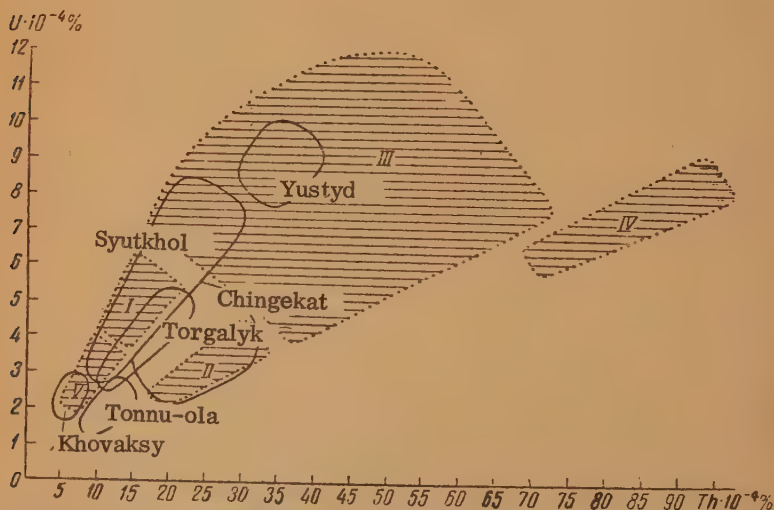


Fig. 4. The position of the granitoids of Central and Western Tuva among L. V. Komlev's radiochemical types of granite massifs (the latter are marked by Roman numerals and outlined by dotted line)

2. The granites of the Chugekat complex, on the other hand, have a somewhat lower Th/U ratio as compared with the granitoids of type II.
3. The granites of the Khovaksy complex correspond to the least radioactive varieties of the granitoids of type V.
4. The granitoids of the Torgalyk complex occupy a more or less intermediate position among the granites of types I, II and V.
5. The main mass of granites of the Syutkhol' complex corresponds to the granites of type I, although the more radioactive massifs of the complex should be referred to massifs of type III, the so-called rare metal type.
6. The granites of the Yustyd complex belong entirely to the rare metal type.
7. There are no granite massifs in Central and Western Tuva which even remotely resemble massifs of type IV.
8. The more general conclusions concerning regional radiochemical characteristics of Tuva are as follows:
8. The granitoids of Central and Western Tuva belong entirely to the types with low and medium radioactivity.
9. Predominant among the granites of Tuva are rocks with average or rather low uranium and thorium content and a somewhat higher than normal thorium-uranium ratio.

## REFERENCES

- Kuznetsov, V. A. and G. V. Pinus (1949). Doklady, 15, No. 1, Izd. Akad. Nauk SSSR.
- Leont'ev, L. N. (1956). Kratkii Geologicheskii Oчерk Tuvy (Brief geological sketch of Tuva), Izd. Akad. Nauk SSSR.
- Ivanova, T. N. and N. I. Polevaya (1956) O Vozraste Intruzii Syutkhol'skogo Kompleksa Tuvy (On the age of the Syutkhol intrusives of Tuva). Inform. sb. Vses. N.-i. geol. in-ta, No. 4.
- Nikolaev, V. A. (1953). Izvestiya, ser. geol., No. 2, Izd. Akad. Nauk SSSR.
- Bilibin, Yu. A. (1955) Metallogenicheskie Provintsii i Metallogenicheskie Epokhi (Metallogenetic provinces and epochs). Gosgeoltekhizdat.
- Vinogradov, A. P. (1955) Zakonomernosti Raspredeleniya Khimicheskikh Elementov v Zemnoi Kore (The regularities of distribution of the elements in the earth's crust). Doklady na yubileinoi nauchnoi sessii MGU, 9-13/V-1955, Izd. MGU.
- (1955) Radiometricheskie Metody Poiskov i Razvedki Uranovykh Rud (Radiometric methods of prospecting for uranium ores). Gosgeoltekhizdat.
- Uklonskii, A. S. (1955) Geokhimicheskoe Znachenie Paraelementov (Geochemical significance of paraelements). Zap. Uzbeksk. otd. Vses. mineralog. o-va, vyp. 8, 18.
- Sheinmann, Yu. M. (1956) Nekotorye Zakonomernosti Rasprostraneniya Vulkanicheskikh Yavlenii na Platformakh (Certain regularities of distribution of volcanic phenomena on platforms). Tr. VAGT'a, vyp. 2.
- Evans, R. D. and C. Goodman (1941) Radioactivity of rocks. Bull. Geol. Soc. Am., 52, p. 459.
- Larsen, E. S. and N. V. Keevill (1947) Radioactivity of the rocks of the batholith of Southern California. Bull. Geol. Soc. Am, 58, p. 483.



12. Strutt, P. S. (1905). Proc. Roy. Soc. (A), 76, p. 88.

1385

Received for publication  
December 16, 1958.

# ON THE PECULIARITIES OF EVOLUTION OF THE ROCKS OF THE KRIVOI ROG SERIES RESULTING FROM ALKALI METASOMATISM

I. V. ALEKSANDROV

V. I. Vernadskii Institute of Geochemistry  
and Analytical Chemistry,  
Academy of Sciences USSR, Moscow

The paper discusses certain characteristics of alkali metasomatism in the rocks of the Krivoi Rog series revealed by diagrams of their chemical composition (Fig. 3).

Investigations of the chemistry of metasomatism usually begin by comparing the composition of the initial and the altered rocks. From this, the amount of rock substance added and removed and the capacity of different elements for migration can be evaluated. Usually one or two analyses of the unaltered rock are compared with one or two analyses of the altered rock. But the use of such a small number of analyses may easily lead to error in dealing with the rocks of the Krivoi Rog series, in which the chemical composition of rocks containing the same mineral assemblage varies within broad limits and direct change from the initial to the metasomatized rock is very seldom observed. In the present paper, an attempt is made to determine the change in composition of the rocks by using a larger than usual number of analyses and attacking the problem statistically with the aid of the diagrams presented below.

## The Principle of Construction of the Diagrams

The weight percentages were recalculated to the relative numbers of cations. Then from the sum of the relative numbers of cations, Si, Al,  $\text{Fe}^{3+}$ ,  $\text{Fe}^{2+}$ , Mg, Ca, Na, K and C (from  $\text{CO}_2$ ), the percentages of these cations were calculated. This procedure is basically similar to one of the methods of calculation proposed by T. Barth ([1], p. 163). The recalculated analyses of the rocks were plotted on the diagrams. On all diagrams, the sum of the percentages of  $\text{Fe}^{3+}$  and  $\text{Fe}^{2+}$  was plotted on the axis of the abscissas. The sum of  $\text{Fe}^{3+}$  and  $\text{Fe}^{2+}$  was selected because: a) iron content in the rocks varies more than the content of any other element (from 1 to 79%) and therefore the analyses are spread over a large interval on the

axis of the ordinates, and b) iron is one of the most inert elements during metasomatism. The diagram  $\text{Ca} - (\text{Fe}^{3+} + \text{Fe}^{2+})$  is omitted because the calcium content in the investigated rocks is low (usually less than 2% by weight).

The rocks are divided into groups according to their petrographic characteristics. On the diagrams, the areas containing analyses of each group are bounded by closed contours. For convenience the contours may be outlined in different colors.

The analysis numbers are given on the diagram  $\text{Fe}^{3+} - (\text{Fe}^{3+} + \text{Fe}^{2+})$ . They are omitted from other diagrams because a given analysis has the same ordinate in every diagram. In each group the consecutive analysis numbers increase with increase in iron content. The consecutive numbers of the metamorphic rocks are the same as those given in a previous paper on this subject [2].

Diagrams aid in geochemical investigations of metasomatism based on petrochemical data and provide material for physicochemical study of the process. Diagrams aid in: a) establishing the relation between petrographic and chemical composition of the rocks, b) determining chemical change in the rocks produced by metasomatism and c) establishing mutual relationships in the behavior of different elements. In the construction of the diagrams the author used the data of Ya. N. Belevtsev, V. S. Domarev, R. P. Dubinkina, A. P. Nikol'skii, Z. V. Novikova, R. P. Petrov, A. S. Pavlenka, N. P. Semenenko, A. I. Tugarinov, M. S. Tsybul'skaya, S. P. Chumakova, I. V. Alexandrov and others.

#### Brief Description of the Geologic Structure of the Metasomatized Areas

The Precambrian Krivoi Rog series is divided into three formations. The basal formation is composed of arkosic sandstones, quartzites and phyllites. The middle formation consists of alternating schists and iron-bearing beds, the former being represented by mica, chlorite and amphibole schists and the latter by ferruginous quartzites and quartz-magnetite-amphibole schists. The upper formation is composed of mica and chlorite schists, quartzites and carbonate rocks.

The rocks of the Krivoi Rog series are crumpled into large isoclinal folds and are traceable, with interruptions, for 230 km in the form of bands striking nearly north-south. Locally there are latitudinal undulations and flexures. Metasomatism is related to the development of some of these flexures.

Four areas of alkali metasomatism are known. All of them lie essentially in the rocks of the middle formation. The structural features of each of the areas are given below (from north to south) \*.

The Kremenchug belt (Fig. 1). Metasomatism is developed on the eastern limb of the Galeshchinsk syncline in the area complicated by flexures. Both along the strike and with depth the metasomatites merge

---

\* Based on the data of Y. N. Belevtseva, D. F. Loginova, K. P. Lyashchenko, R. P. Rotshteina, N. P. Semenenko, N. K. Stekhina, G. F. Ferina, I. V. Aleksandrova and others.

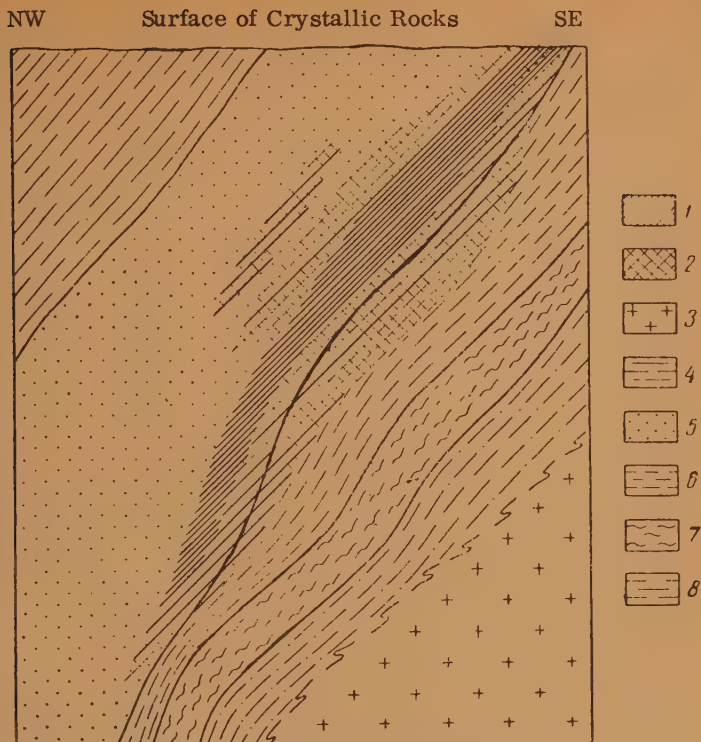


Fig. 1. Diagrammatic geologic section of the metasomatized area in the Kremenchug belt

1 -- silica-limonite rocks, 2 -- alkali and carbon dioxide metasomatism, 3 -- granites

#### Krivoi Rog series

4 -- 4th schist horizon of the middle formation,  
5 -- 3d ferruginous horizon of the middle formation,  
6 -- lower part of the middle formation,  
7 -- talc horizon, 8 -- lower formation

to metamorphic rocks. Silica-limonite rocks have developed at the expense of the metasomatites.

The Zheltorechensk belt. The rocks of the core and limbs of the Zheltorechensk syncline were subjected to alkali metasomatism near a large transverse flexure in its trough.

The Annovsk belt (Fig. 2). The alkali metasomatism affected the rocks of the core and limbs of the Annovsk syncline near a transverse complication of its trough.

The Northern part of the Saksagan belt. In the northern part of the



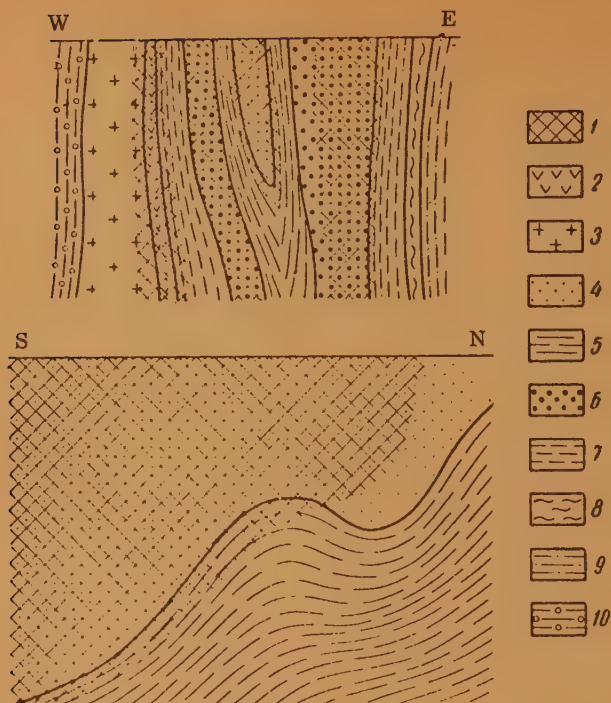


Fig. 2. Diagrammatic geologic section of the metasomatized area in the Annovsk belt

1 -- alkali metasomatism, 2 -- amphibolites, 3 -- granites

#### Krivoi Rog series

4 -- 2nd ferruginous horizon of the middle formation, 5 -- 2nd schist horizon of the middle formation, 6 -- 1st ferruginous horizon of the middle formation, 7 -- 1st schist horizon of the middle formation, 8 -- talc horizon, 9 -- lower formation, 10 -- gneisses (older than the Krivoi Rog series)

Saksagan belt the northeast trending eastern limb of the Saksagan syncline turns almost 90° and strikes northwest. At the bend, the rocks of the Krivoi Rog series are broken into a number of strongly overthrust blocks. One of these blocks, composed of ferruginous quartzites, is intensively metasomatized. The manifestations of alkali metasomatism in the other areas of the region are negligible.

Table 1

Metamorphic rocks	Products of alkali metasomatism	Products of carbon metasomatism
<u>Kremenchug belt</u>		
Ferruginous quartzites	Alkali amphibole-aegirine rocks (aegirine, alkali amphiboles, magnetite, martite)	Carbonatized alkali amphibole-aegirine rocks
Magnetite-amphibole-chlorite schists	Alkali amphibole schists (alkali amphiboles, magnetite, sometimes hydrobiotite)	Carbonatized alkali amphibole schists
<u>Zheltorechensk belt</u>		
Ferruginous quartzites and quartz - magnetite-amphibole schists	Magnetite-alkali amphibole-aegirine rocks	Magnetite-martite-aegirine-carbonate rocks
Mica schists	Mica and chlorite-albite schists and albitites	
<u>Annovsk belt</u>		
Ferruginous quartzites	Magnetite-alkali amphibole-aegirine rocks and aegirinites	Vein albitites
Quartz-magnetite-amphibole schists	Magnetite-alkali amphibole schists	
Amphibolites and biotite-amphibole schists	Albite-hydrobiotite-alkali amphibole schists	
Mica schists	Mica-chlorite-albite schists and albitites	
<u>Northern part of the Saksagan belt</u>		
Ferruginous quartzites and quartz magnetite-amphibole schists	Magnetite-alkali amphibole-aegirine rocks, magnetite-alkali amphibole schists	Magnetite-martite-alkali amphibole-aegirine-carbonate rocks
	Alkali amphibole-magnetite ores	Alkali amphibole-carbonate-magnetite-martite ores
	Infrequent carbonate-albite veinlets and albitization of mica and amphibole schists	

The most typical metasomatic changes in the metamorphic rocks are listed in Table 1.

In all areas rather thick beds, sometimes entire members of the formation, were subjected to alkali metasomatism, but the boundaries between the beds and members were preserved. Bed-like bodies of metasomatites 1 - 2 km in length were formed which often contain beds of unaltered or slightly altered rocks (Fig. 2). Later, in the fractures of the bed-like metasomatic rocks, vein metasomatites were formed.

To make what follows understandable, two points must be clarified.

First. Let us attempt to answer the question: where did the metasomatic solutions come from?

This may be determined in part by an analysis of the geological setting. Inasmuch as only a brief description has been given of the geologic structures, the author's ideas can be presented in only a very generalized form.

It is known that along the strike the metasomatites are replaced by metamorphic rocks. At present it is known from deep drilling that this change occurs also with depth (Fig. 1). The metasomatic rocks are evidently surrounded by metamorphic rocks. It must be assumed, therefore, that the solutions came to the metasomatized areas directly from the metamorphic rocks.

In a previous paper [2] it was noted that solutions played an important role during metamorphism ("pore solutions, metamorphic solutions") and that between the metamorphic rocks and the solutions there existed a state approaching equilibrium. It follows from this that the metamorphic rocks of different composition contained solutions different in composition; for example, the content of certain elements in solutions in the ferruginous and schistose horizons was different. These are the first and very general ideas concerning the solutions which, as the author supposes, participated in metasomatism.

The development of the transverse flexures mentioned above was accompanied by fracturing, which released pressure in these areas and increased the rate of percolation of solutions. Inasmuch as the metasomatites are, in general, bed-like, it is natural to assume that the solutions flowed mainly between beds or members.

Metasomatism occurred when the equilibrium between the rocks and the solutions was disturbed, and continued until under new conditions near-equilibrium was attained once more.

For the present we shall limit ourselves to these remarks and suppositions. Later, after further examination of the data, we shall check them and consider other questions concerning solutions.

The second point concerns the mobility and inertness of certain elements.

In what follows we shall adhere to the following definition of inert and completely mobile components: "If in all reactions between the rock and the solutions the concentration of certain components in the solution is maintained at some constant arbitrary level, due either to the introduction of material from the outside or to its removal, these components are considered completely mobile. The inert components are those whose concentration in the solutions is determined by the saturation of the solution with the rock substance" ([3] p. 38).

It should be noted that removal of an element by percolating solutions is always related to an increase in its concentration in the area of metasomatism, while introduction of an element is always related to a decrease in its concentration.

Introduction or removal of an element does not mean that this element becomes either inert or completely mobile, but merely that it becomes more mobile or more inert. If, with the increase in concentration of an element (for example, due to a change in the pH of the solution) the concentration were still determined by the saturation of the solution with the rock material, the mobility of this element would increase but it would remain inert.

Let us pass now to the main subject of the paper.

Rocks of different composition are formed by metasomatism (Table 1). This is due to the effect of several factors on the metasomatic process, of which the following will be discussed: 1) the effect of composition of the initial metamorphic rocks, 2) the effect of temperature, 3) the effect of the rate of percolation of solutions and 4) the effect of the composition of the solutions. At the same time, we shall determine the direction in which the composition of the rocks was changed and the behavior of the rock-forming minerals during metasomatism.

### 1. THE EFFECT OF COMPOSITION OF THE ORIGINAL METAMORPHIC ROCKS. THE CHANGES IN THE MINERALOGICAL AND CHEMICAL COMPOSITION OF THE ROCKS

Let us review the changes which took place in the mica schists, quartz-magnetite-amphibole schists and amphibole-magnetite quartzites.

#### a) Mica Schists.

The most typical mineral assemblage in these rocks is quartz-biotite-muscovite-chlorite. Some varieties of schists contain plagioclase (oligoclase, albite-oligoclase), sillimanite and garnet (almandine).

Metasomatic changes consisted in partial replacement of chlorite, recrystallization of muscovite and complete replacement of quartz and biotite by albite. Quartz was replaced more fully and earlier than biotite. As a result, chlorite-muscovite-albite schists were formed, occasionally containing relicts of biotite. Under more intensive metasomatism, chlorite and muscovite were replaced by albite, sometimes so completely that monomineralic albitites were formed.

Analyses 8 - 12 on the diagrams (Fig. 3) represent mica schists of the Zheltorechensk belt [2] and analyses 76-81, albitites formed after mica schists in the same region.

The Zheltorechensk albitites are either monomineralic or carry a small amount of alkali amphiboles, aegirine and hematite in the areas with high iron content.

The formation of monomineralic albitites after mica schists is a common phenomenon. The high iron content is due in most cases to a slight addition of the element from the neighboring ferruginous horizon also subjected to intensive metasomatism.

In the upper part of the contour (Fig. 3) are nearly monomineralic albitites (analyses 76-79). A slight reduction in the Si content occurred during their formation at the expense of mica schists. No significant change is observed in the content of aluminum. Aluminum is abundant both in the original rocks and in the metasomatites. Evidently in some cases the amount of aluminum was either slightly diminished (for example in schists rich in micas) or slightly increased (for example in schists relatively poor in micas). The iron content does not show significant changes either. In



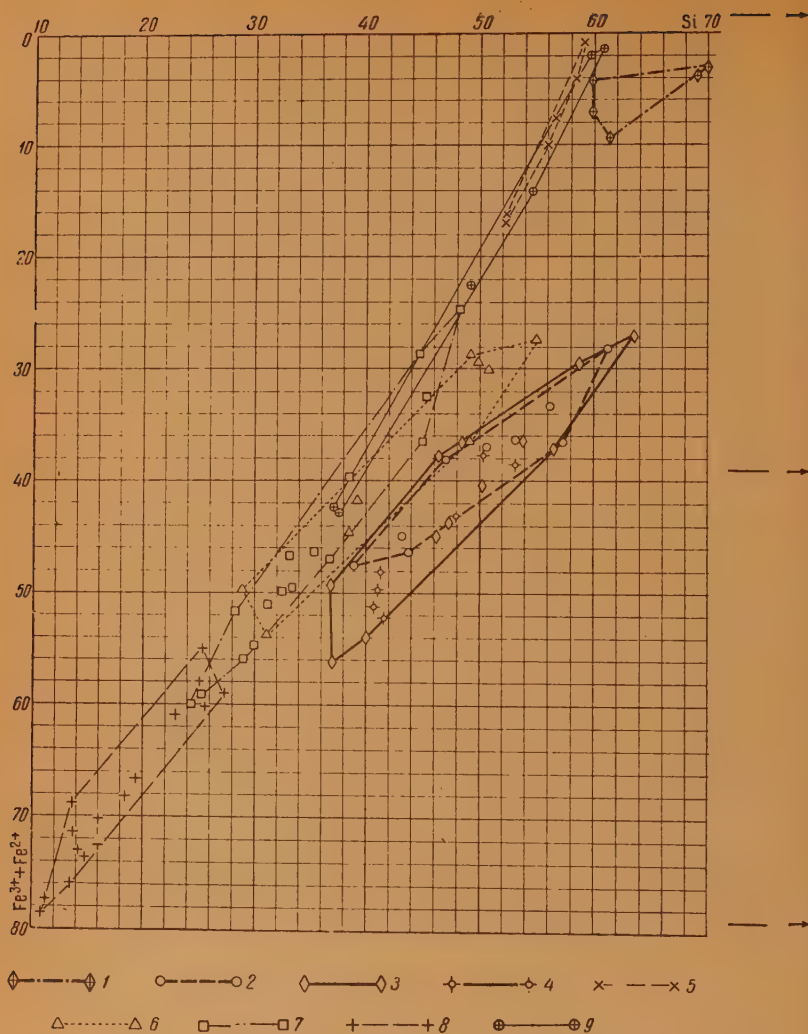


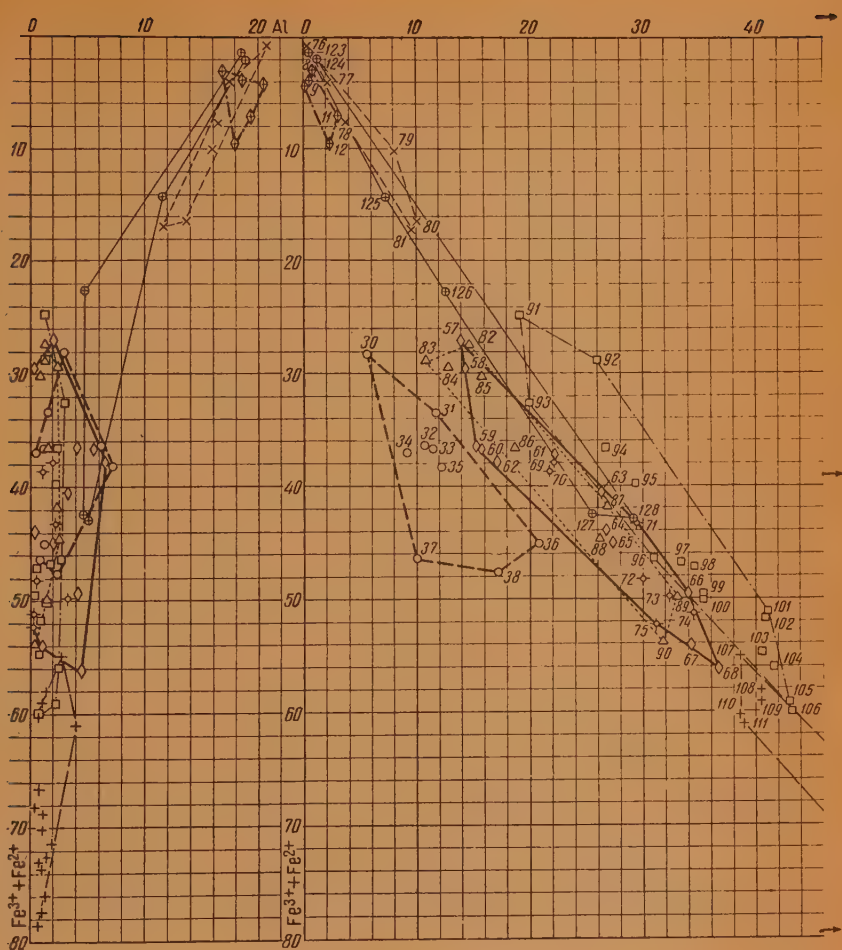
Fig. 3. Chemical composition of the metamorphic rocks of the Krivoi Rog series and of the metasomatic rocks formed from them

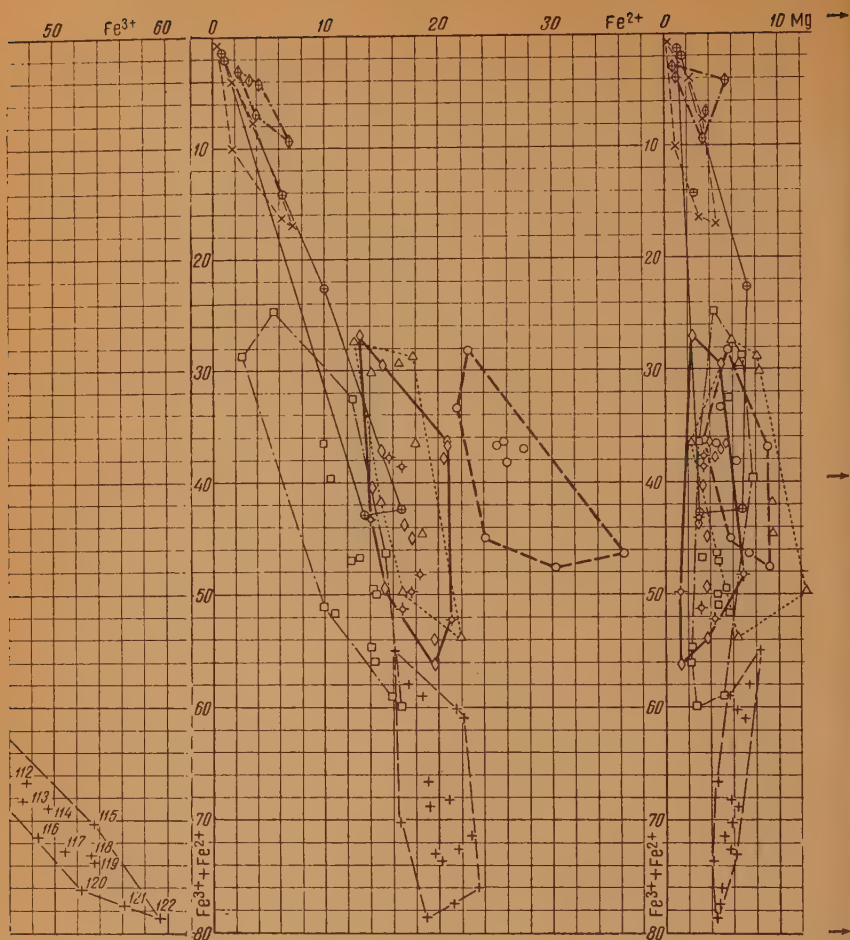
Metamorphic rocks

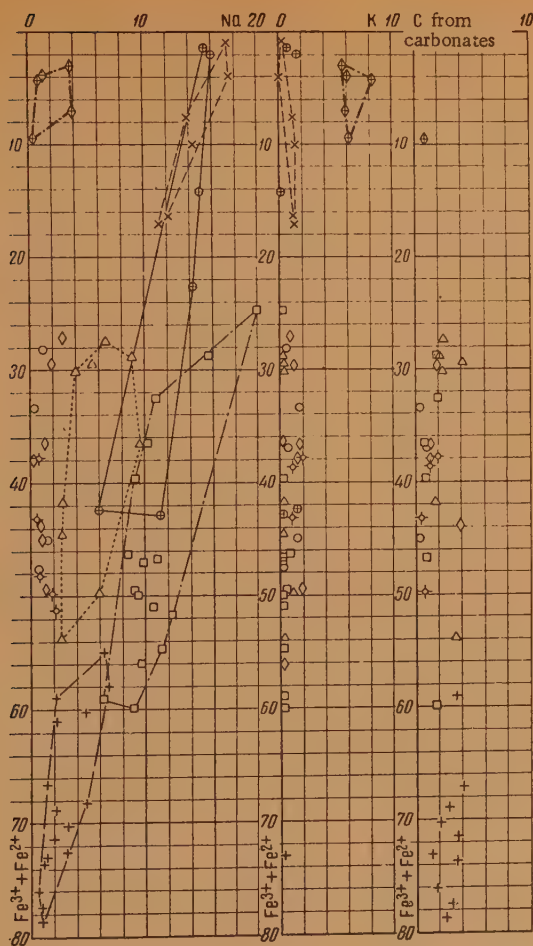
- 1 -- mica schists, 2 -- quartz-magnetite-amphibole schists,  
3 -- magnetite-amphibole quartzites, 4 -- amphibole-  
pyroxene-magnetite quartzites;

Metasomatic rocks

- 5 -- albitites, 6 -- magnetite-alkali amphibole schists, 7 --  
aegirinites, and magnetite-alkali amphibole aegirine rocks,  
8 -- alkali amphibole-magnetite ores, 9 -- albitized aegiri-  
nites and magnetite-alkali amphibole-aegirine rocks









the mica schists  $\text{Fe}^{2+}$  predominates over  $\text{Fe}^{3+}$ , while in the albitites the situation is reversed. In mica schists with relatively high Mg content its amount was decreased by metasomatism. The content of Na increased considerably while that of K decreased.

As compared with the monomineralic albitites, those containing alkali amphiboles, aegirine or hematite (lower part of the concentration contour), have less Si, Al and Na and more Fe; the increase in the content of  $\text{Fe}^{3+}$  is more pronounced than in the  $\text{Fe}^{2+}$  content.

b) Quartz-magnetite-amphibole schists.

The schists are composed of cummingtonite-grunerite, magnetite, quartz, biotite and, less frequently, alkali amphiboles and garnet (almandine). In the rocks of the relatively low metamorphic rank, chlorite is typical and siderite is present. The most common paragenesis is amphibole-magnetite-quartz-biotite.

The alkali metasomatism caused a strong enrichment of the cummingtonite-grunerite in the alkalis, replacement of quartz and biotite by fine-grained alkali amphiboles and hydrobiotite, and partial martitization of magnetite. As a result, magnetite-alkali amphibole schists were formed containing subordinate amounts of hydrobiotite and martite. The alkali amphiboles are rhodosite, riebeckite and, less often, galucophane. Aegirine is absent from these schists, or occurs in very small amounts.

In the Kremenchug belt, during carbon dioxide metasomatism, which followed alkali metasomatism, the alkali amphiboles in the magnetite-alkali amphibole schists were replaced by the carbonates (dolomite, calcite, ankerite) and martitization was more intensive.

On the diagrams (Fig. 3), the quartz-magnetite-amphibole schists are represented by analyses 30 - 38 [2] and the magnetite-alkali amphibole schists formed from them, by analyses 82-90 (Table 2).

The following changes in the chemical composition of the quartz-magnetite-amphibole schists were caused by alkali metasomatism: the content of Si decreased, the Fe content remained nearly the same but a part of the  $\text{Fe}^{2+}$  was oxidized, the Mg content increased slightly and Na content, considerably.

c) Amphibole-magnetite quartzites.

The ferruginous quartzites are composed of the following minerals: quartz, magnetite, cummingtonite-grunerite, biotite and alkali amphiboles. In some varieties of quartzite there are also coarse-grained aegirine or aegirine-diopside, microcline and plagioclase. Typical of the relatively weakly metamorphosed rocks are hematite, siderite and stilpnomelane. The most common paragenesis is: quartz-magnetite-amphibole-biotite.

During alkali metasomatism, aegirine replaced quartz and biotite completely and magnetite in part. The latter was also slightly martitized. A fibrous alkali amphibole was formed together with aegirine. Alkalies were introduced into cummingtonite-grunerite. The resulting rocks were aegirinites and magnetite-alkali amphibole-aegirine rocks.

Often the aegirine and alkali amphibole metamorphic rocks which have regional distribution are regarded as products of alkali metasomatism. These rocks are characterized by the following association: quartz-magnetite-aegirine-alkali amphiboles-micas and sometimes microcline. In the present paper only the locally developed rocks associated with areas of structural complication are considered as the products of alkali metasomatism. Their characteristic paragenesis is: aegirine-alkali amphiboles-magnetite. No quartz, micas or microcline are present inasmuch as they are unstable and are, as a rule, completely replaced. The difference

Table 2

Chemical Analyses of Rocks wt. % 1958

	83	86	89	91	110
SiO <sub>2</sub>	48,78	46,35	26,84	50,15	23,24
TiO <sub>2</sub>	0,10	0,12	0,35	0,45	0,51
Al <sub>2</sub> O <sub>3</sub>	1,07	1,23	1,13	1,19	0,46
Fe <sub>2</sub> O <sub>3</sub>	14,34	23,51	40,48	26,46	44,35
FeO	21,17	20,30	19,12	6,80	22,26
MnO	0,11	0,05	0,03	0,08	0,03
MgO	5,43	1,54	7,91	3,10	3,58
CaO	1,03	0,56	0,15	1,13	1,70
Na <sub>2</sub> O	4,50	4,76	2,90	10,70	2,01
K <sub>2</sub> O	0,28	0,38	0,78	0,20	0,34
CO <sub>2</sub>	1,47	—	Her	—	—
H <sub>2</sub> O	1,45	1,08	0,78	0,31	1,51
Total	99,73	99,88	100,47	100,57	99,99

Note: Comma represents decimal point.

Note. 83. Rhodusite schist. Composed of fibrous rhodusite containing magnetite dust. Occasionally long prisms of incompletely alkalinized cummingtonite are observed, slightly carbonatized in some areas. Kremenchug belt. I. V. Aleksandrov, analyst.

86. Riebeckite schist. Composed mainly of riebeckite which replaced cummingtonite-grunerite prismatic grains. Fine-grained and fibrous riebeckite is also found. Secondary mineral is magnetite. Infrequently riebeckite is replaced by fibrous aegirine. Annovsk belt. I. V. Aleksandrov, analyst.

89. Martite-magnetite-rhodusite schist. Composed of fine-grained and fibrous rhodusite and martitized magnetite. Some hydrobiotite in small scales. Zheltorechensk belt. I. V. Aleksandrov, analyst.

91. Aegirinite. The rock is composed essentially of cryptocrystalline and fibrous aegirine. Associated mineral is alkali amphibole formed at the expense of cummingtonite-grunerite. Occasional magnetite grains and small albite veinlets. I. V. Aleksandrov, analyst.

110. Hydrobiotite-hematite-magnetite-alkali amphibole rock. Albite is present in small amounts. Zheltorechensk belt. A. V. Zmeenova, analyst.

in parageneses points to a difference in the chemistry of the process.

In the Kremenchug belt, in the northern part of the Saksagan belt and, to a less extent, in the Zheltorechensk belt, during the carbon dioxide metasomatism which followed alkali metasomatism, the carbonates (dolomite, ankerite, calcite) replaced the alkali amphiboles and aegirine. These latter were recrystallized during the process. Martitization of magnetite increased.

Magnetite-amphibole and amphibole-pyroxene-magnetite quartzites are represented on the diagrams by analyses 57-75 [2], and aegirinites and magnetite-alkali amphibole-aegirine rocks (analyses 91-106) formed from them, with aegirine predominating over alkali amphiboles.

As a result of metasomatism, the content of Si in the ferruginous quartzites diminished. The iron content did not change noticeably. Ferrous iron was partially oxidized, usually just enough to provide for the formation of alkali silicates. Oxidation during martitization was negligible as compared with that in the preceding case. The content of Al diminished in the ferruginous quartzites, which are relatively rich in Al due to the replacement of micas. Mg content did not change, but Na content increased substantially.

On the Si -- ( $\text{Fe}^{3+} + \text{Fe}^{2+}$ ) diagram, the concentration contours of the aegirine-bearing metasomatites and ferruginous quartzites come together in the lower part but separate somewhat in the upper part. This is explained by the fact that the formation of aegirine was accompanied by removal of Si. The more aegirine that was formed (upper part of the concentration contour), the more Si was removed.

The same diagram shows that the contour of the aegirine-bearing metasomatites is shifted somewhat to the left relative to that of the magnetite-alkali amphibole schists. The analyses of the latter, except for 87 and 89, lie to the right side of the contour of the magnetite-alkali amphibole-aegirine rocks. According to the conditions of its formation, rock 89 should really be referred to the magnetite ores which will be discussed below. It is placed with the magnetite-alkali amphibole schists because in it, alkali amphiboles noticeably predominate over iron ores. The relationship of the schists to the magnetite-alkali amphibole-aegirine rocks means that, in general, during the formation of aegirine-bearing metasomatites more Si was removed than during the formation of magnetite-alkali amphibole schists; i.e., in the first case, the concentration of Si in the solutions in the area of metasomatism increased more than in the second case. Therefore, aegirine, all other conditions being equal, developed at a higher concentration of Si than did alkali amphiboles.

This may be explained in the following way. Of all the minerals containing Si, quartz was the least stable, and during alkali metasomatism was not in equilibrium with the solutions. In other words, the solutions were undersaturated in Si with respect to quartz. Therefore, all other conditions being equal, the more quartz present in the rock, the greater became the concentration of Si in the solutions. The amphibole-magnetite quartzites contain more quartz than the quartz-magnetite-amphibole schists. Therefore, the concentration of Si in solutions reacting with ferruginous quartzites increased more than in solutions reacting with quartz-magnetite-amphibole schists, and this favored the formation of aegirine.

## 2. THE EFFECT OF TEMPERATURE

First of all, was there a change in temperature during metasomatism?

We shall try to answer this question by comparing the sequence of formation of minerals during metasomatism and during progressive metamorphism. The latter, as is well known, occurs with rising temperature. In progressive metamorphism, siderite and hematite formed in the ferruginous rocks at an early stage become unstable and are replaced by amphiboles, aegirine and magnetite [2].



At an early stage of metasomatism, i.e., alkali metasomatism, aegirine and alkali amphiboles formed abundantly in the rocks. Weak martitization began. Later, during carbon dioxide metasomatism, which follows alkali metasomatism, aegirine and the alkali amphiboles were replaced by carbonates, and the martitization of magnetite became more intensive.

Therefore, metasomatism presents a reverse pattern as compared with progressive metamorphism. This suggests that metasomatism occurred, in general, with decreasing temperature.

The metasomatized areas are not isolated from the metamorphic rocks surrounding them. It is natural to suppose that the lowering of temperature is related to a general temperature decrease in the rocks of the Krivovir Rog series, i.e. that metasomatism occurred against a background of retrogressive metamorphism.

Another question arises: were temperature differences which existed during metamorphism in the four areas investigated preserved during metasomatism?

The least metamorphosed rocks are found in the Kremenchug belt and in the northern part of the Saksagan belt. Here no plagioclase was formed in the mica schists. Amphiboles did not completely replace chlorite in the amphibole-chlorite schists, and the ferruginous quartzites contain siderite and bands of fine-grained hematite.

In the Zheltorechensk belt, where metamorphism was more intensive, plagioclase often occurs in the mica schists, and siderite and fine-grained hematite are usually absent from the ferruginous quartzites.

Still more intensive metamorphism is exhibited by rocks of the northern part of the Annovsk belt where the metasomatized area is located. The mica schists contain plagioclase and sometimes sillimanite. In amphibole schists formed at the expense of chlorite schists, chlorite is completely replaced by amphiboles, and siderite and fine-grained hematite are completely absent from the ferruginous quartzites.

Thus, the highest temperature during progressive metamorphism existed in the Annovsk belt; the lowest, in the Kremenchug belt and in the northern part of the Saksagan belt.

Now let us compare the degree of development of the metasomatic minerals in the different areas.

Aegirine and alkali amphiboles occur in all four areas. Albite is widely developed in the metasomatites of the Annovsk and Zheltorechensk belts and relatively weakly in the Kremenchug belt and the northern part of the Saksagan belt. Carbonates are very rare in the metasomatites of the Annovsk belt, common in the Zheltorechensk belt and very abundant in the metasomatites of the Kremenchug belt and the northern part of the Saksagan belt. Hematite (martite) is weakly developed in the metasomatites of the Annovsk belt, rather widely in the Zheltorechensk belt and still more extensively in the Kremenchug belt and the northern part of the Saksagan belt.

After comparing the development of albite, the carbonates and hematite (martite) in the metasomatites of the different areas with the development of plagioclase, carbonates and hematite during the different stages of metamorphism, we may conclude that the highest temperatures existed during metasomatism in the Annovsk belt, relatively low temperatures in the Kremenchug belt and in the northern part of the Saksagan belt, and intermediate in the Zheltorechensk belt. The formation of minerals during progressive metamorphism in this area is discussed in greater detail in the paper by I. V. Alexandrov and A. V. Zmeenkova [2].

It is evident that metasomatism in the different areas occurred at



different temperatures and that, as during metamorphism, the highest temperatures were reached in the Annovsk area, while the lowest temperatures obtained in the Kremenchug and Saksagan areas.

This leads to the conclusion that metasomatism occurred during the earlier stages of retrogressive metamorphism, when the temperature differences established during progressive metamorphism between different areas still existed.

### 3. THE EFFECT OF THE RATE OF PERCOLATION OF SOLUTIONS

Besides aegirinites and magnetite-alkali amphibole-aegirine rocks, alkali metasomatism of ferruginous quartzites also produced alkali amphibole-magnetite ores. The formation of these ores involved the addition of alkalis to cummingtonite-grunerite, the development of fine-grained alkali amphiboles (rhodusite, riebeckite), the disappearance of quartz, the partial martitization of magnetite and the appearance of subordinate amounts of hydrobiotite. Sometimes the ores contain hematite. Aegirine is absent, or present in small amounts.

The zones of alkali amphibole-magnetite ores are from 2 to 20-30 meters thick and several hundred meters long. They lie among other metasomatites, usually passing along the strike and with depth into magnetite-alkali amphibole-aegirine rocks.

The ores are widely developed in the metasomatic area of the northern part of the Saksagan belt. They occur also in the Zheltorechensk and Annovsk belts.

On the diagrams the ores are represented by analyses 107-122.

The alkali amphibole-magnetite ores are the products of the same process as the magnetite-alkali amphibole schists and magnetite-alkali amphibole-aegirine rocks. All these rocks are closely associated in space and are composed of the same minerals.

The diagram shows that the formation of alkali amphibole-magnetite ores at the expense of ferruginous quartzites was accompanied by a considerable decrease in silicon content and a large increase in iron content. Such sharp change in the composition of the rocks as compared with the normal was caused, perhaps, by a more intensive percolation of solutions in some zones and the resulting intensified migration of matter.

Evidently large amounts of silicon were removed, for, as has already been shown, this is a characteristic feature of metasomatism. The problem of iron enrichment is more complex. The considerable increase in iron content can be explained either by the introduction of large amounts of iron or the enrichment of the rocks, mainly as a result of removal of silicon. Let us consider these two possibilities.

The formation of ores as a result of the introduction of large amounts of iron would mean its increased mobility in the percolating solutions and loss of mobility in the metasomatic areas. If iron had high mobility in the solutions, it would have been introduced not only into the ores but into other metasomatic rocks as well. This is not so, for in most metasomatites the content of iron is not higher than in the original rocks.

Thus, it is more likely that the substantial enrichment in iron occurred not because considerable amounts of iron were introduced but because silicon was removed. The volume of the rocks was evidently reduced as a

result of the removal of Si.

Interesting information on the origin of rich hypogene iron ores in the region of the Kursk magnetic anomaly is found in the paper by A. A. Glagolev [4]. The author cites data in favor of the formation of ores from ferruginous quartzites as a result of solution and removal of silica and concentration of iron. The volume of the rocks was reduced by about 50%.

Let us continue our examination of the diagrams. When the ores were formed from aluminum-rich ferruginous quartzites, the content of Al was slightly reduced. In other cases the Al content was not noticeably changed. The content of Mg increased. The content of Ca in the ores also increased slightly as compared with the ferruginous quartzites. Sometimes this was due to the presence in the samples of small admixtures of carbonates (dolomite and calcite) which formed during later carbon dioxide metasomatism. The formation of the alkali amphiboles in the ores resulted in an increase in sodium content.

Let us consider one more question. Why did alkali amphiboles but not aegirine form in the iron ores?

It was noted above that higher concentrations of Si in the solutions are needed for the formation of aegirine than for the formation of alkali amphiboles. In the ore zones the concentration of Si, in most cases, was not sufficient for the formation of aegirine because of the relatively rapid percolation of solutions and unusually rapid removal of silicon.

On the diagrams the concentration contours of the alkali amphibole-magnetite ores are continuations of the contours of the magnetite-alkali amphibole schists. This is quite natural, because both varieties of rocks are composed of the same minerals except that in the first, iron ore minerals predominate, and in the second, alkali amphiboles.

The lower part of the concentration contour of the magnetite-alkali amphibole-aegirine rocks on the diagram Si -- ( $\text{Fe}^{3+} + \text{Fe}^{2+}$ ) unites with the contour of the magnetite-alkalic amphibole schists. A boundary is drawn between the schists and the alkali amphibole-magnetite ores. Above the boundary, during the formation of magnetite-alkali amphibole schists, the removal of Si was less than during the formation of the aegirine-bearing metasomatites, and the concentration of Si in the solution remained insufficient for the development of aegirine. Below this boundary, during the formation of the ores, more silica was carried out than during the formation of the aegirine-bearing metasomatites, but the concentration of Si in the solution, because of its relatively rapid removal, also remained insufficient for the formation of aegirine.

The magnetite-alkali amphibole-aegirine rocks and the alkali amphibole-magnetite ores were formed at the expense of the same rocks in the same beds and at the same time. Therefore, there is no reason to suppose that the differences in their composition are related to the differences in the acidity or alkalinity of the solutions.

Let us note that the formation of aegirine and alkali amphiboles depends on many factors and while, during the alkali metasomatism of the Krivoi Rog series, the principal role in the preferential development of one or the other of these minerals was played by difference in the concentration of Si, elsewhere other factors might have played the principal role, among them differences in the acidity or alkalinity of the solutions.

#### 4. THE EFFECT OF THE COMPOSITION OF THE SOLUTIONS

Sometimes veins and vein-like bodies of metasomatic albitites developed

at the expense of aegirinites and magnetite-alkali amphibole-aegirine rocks. This occurred on the largest scale in the Annovsk belt in the second iron-bearing horizon lying in the core of the syncline (Fig. 2), where, during alkali metasomatism, fractures and fracture zones ranging from a few tens to several hundred meters in length admitted alumina-rich solutions from the underlying schists.

On the diagrams, analyses 123-128 represent albitized aegirinites and magnetite-alkali amphibole aegirine rocks of the Annovsk belt.

The diagrams show that during the albitization of aegirinites and magnetite-alkali amphibole-aegirine rocks, considerable amounts of silicon and aluminum were introduced, while iron and magnesium was removed from rocks relatively rich in them. Therefore, during the albitization of the aegirine-bearing metasomatites the concentration of Si and Al in the solutions percolating from mica schists was decreased and the concentration of Fe and, in some cases, of Mg increased. Sodium will be considered later. This means that in the solutions existing in the mica schists the concentration of Si and Al was higher and the concentration of Fe and in some cases Mg, lower than in the solutions present in the magnetite-alkali amphibole-aegirine rocks with which aegirine and alkali amphiboles were in equilibrium (Fig. 4).

It was noted earlier that during the formation of aegirinites and magnetite-alkali amphibole-aegirine rocks the concentration of silicon in the solutions percolating through the ferruginous quartzites was increased and that of iron, aluminum and magnesium remained almost unchanged. In other words, in solutions in equilibrium with the ferruginous quartzites, the concentration of Fe, Al and Mg remained approximately the same, while the concentration of Si decreased as compared with the solutions with which the aegirine-bearing rocks were in equilibrium (Fig. 4).

The concentrations of elements in solutions in equilibrium with the ferruginous quartzites and mica schists may now be compared (Fig. 4). It turns out that in solutions in the ferruginous quartzites the concentration of Fe was higher and the concentration of Si and Al lower than in solutions in the mica schists. Therefore, our supposition that solutions of different composition participated simultaneously in alkalic metasomatism is confirmed.

The albitization of ferruginous rocks and the development of aegirine in the mica schists, connected with the mixing of solutions of different composition, are anomalous as compared with the normal aegirinitization of ferruginous quartzites and albitization of mica schists. This indicates that the solutions moved essentially bed by bed, along different horizons.

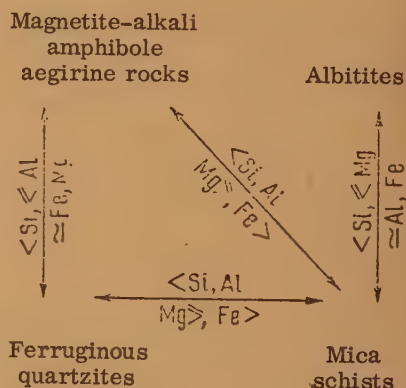


Fig. 4. Comparison of concentrations of Si, Al, Fe and Mg in solutions which were in equilibrium with different rocks



Otherwise, albitization of ferruginous quartzites and development of alkali amphiboles and aegirine in mica schists by mixing of solutions from different horizons would not be an anomalous but a normal phenomenon.

Let us review the behavior of sodium. The sodium content in the metasomatites is determined by their content of albite, aegirine and alkali amphiboles and by the content of Na in these minerals. The dependence of sodium on silicon can be seen on the diagrams. In general, the content of Na increases in every metasomatite with increase in the silicon content. It is not difficult to see that the Si content in albitites, aegirinites and magnetite-alkali amphibole-schists was determined, in its turn, by the silica content of the parent metamorphic rocks. It appears then, that in alkali metasomatism, in each individual case, a certain amount of sodium was withdrawn from the solutions which was needed for the formation of the alkali silicates. This could only occur if an excess of sodium were present in the solutions and if Na were a completely mobile component.

### Summary

The solutions which acted on the metamorphic rocks simultaneously and produced metasomatic changes differed in composition and hence could not have come from a single source such as a magmatic chamber. It is believed that metasomatism was effected by pore solutions present in the metamorphic rocks and that the solutions in the mica schists differed in composition from the solutions in the ferruginous rocks. Metasomatism proceeded with falling temperature during the first stage of retrograde metamorphism. Mica schists were usually changed into albitites and chlorite-muscovite-albite schists; the quartz-magnetite-amphibole schists, to magnetite-alkali amphibole schists; and the amphibole-magnetite quartzites to magnetite-alkali amphibole-aegirine rocks and aegirinites. In the zones of intensive percolation of solutions through the ferruginous quartzites, alkali amphibole-magnetite ores were formed.

Aluminum, iron and magnesium were inert during alkali metasomatism. Their mobility under usual conditions (excluding the case of mixing of solutions) did not change to any extent. The mobility of silicon increased but it remained inert since its concentration in the solutions was determined by the mineralogical composition of the metasomatites (aegirine, alkali amphiboles, albite). Sodium, potassium and carbon dioxide were completely mobile.

Alkali metasomatism in the Krivoi Rog region was characterized by the following features: a) precipitation of sodium, b) removal of Si, c) near immobility of Al, Fe and Mg under ordinary conditions, and d) oxidation of Fe during the formation of aegirine and the alkali amphiboles and, to a smaller degree, during martitization.

This study is not definitive. It contains only those points which it was possible to establish by studying the material cited in the paper.

The research on metasomatism in the Krivoi Rog region was carried out under the guidance of A. I. Tugarinov.

In conclusion, the author extends his thanks to L. V. Dmitriev, A. S. Pavlenko, F. V. Syromyatnikov, A. I. Tugarinov and V. V. Shcherbina for their valuable comments, and to A. V. Shustrov for his help in construction of the diagrams.



## REFERENCES

1. Chetverikov, S. D. (1956) *Rukovodstvo k Petrokhimicheskim perschetam* (Textbook of petrochemical calculations). Gosgeoltekhizdat.
2. Aleksandrov, I. V. (1958). *Geokhimiya*, No. 1.
3. Korzhinskii, D. S. (1936). *Izvestiya, ser. geol.*, No. 1. Izd. Akad. Nauk SSSR.
4. Glagolev, A. A. (1957). *Izvestiya, ser. geol.*, No. 8, Izd. Akad. Nauk SSSR.

Received for publication  
May 21, 1959.

## MINERALOGICAL-GEOCHEMICAL ZONING IN THE IRON DEPOSITS OF THE KONDOMA REGION OF GORNAYA SHORIYA

V. A. VAKHRUSHEV

Institute of Geology and Geophysics of the Siberian Affiliate  
of the Academy of Sciences USSR, Novosibirsk

The Kondoma region of Gornaya Shoriya (Western Siberia) contains the Sheregesh, Shalym, Tashtagol and Kochura iron deposits, long ago united by geologists into a single genetic group. The mineralogy of the skarn ores within the group changes gradually from north to south, i. e. from the high temperature Sheregesh deposit to the southernmost Kochura deposit.

The zonal arrangement of the minerals was mentioned in a general way by N. E. Batov [1], who explained it by variation in the temperature of ore deposition with distance from the igneous source. He regarded the granite of the Sarlyk-Mustag pluton as the parent intrusive.

Later, it was shown that the iron mineralization was genetically related to a syenite complex rather than the granite, and zoning was ascribed by I. V. Derbikov [3] and some other investigators to differences in the depth to which the individual bodies of syenite were eroded. In the direction from the Sheregesha to the Kochura deposit the depth of erosion and the area of exposed syenites decrease, and at the latter deposit they do not outcrop at all.

The discussion of the problem of zoning is based on the author's own investigations, with the data of his predecessors being taken into account. In addition to the minerals of the deposits, the admixed elements in the ores are discussed in detail. The regularities of their distribution in the magnetites of the iron deposits were first established by the author.

The mineralogical zoning within the Kondoma group of iron deposits is sharp. This is illustrated in part by Tables 1 and 2. Table 1 lists the most characteristic gangue mineral assemblages, which, with rare exceptions, are genetically related to the process of skarn-ore deposition. A complete list of the hypogene ores in the order of their abundance in each deposit is given in Table 2.

Table 1 shows that the typical mineral assemblage of the Sheregesh deposit contains anhydrous lime-iron and magnesium-iron silicates of the pyroxene group, and garnets. In addition, there are small amounts of such high temperature minerals as olivine, spinel, scapolite, idocrase and wollastonite.

Table 1\*

Sheregesh	Shalym	Tashtagol	Kochura
Olivine	-	-	-
Wollastonite	-	-	-
Idocrase	-	-	-
Spinel	Spinel	-	-
Scapolite	Scapolite	-	-
Pyroxene	Pyroxene	-	-
Garnet	Garnet	Garnet	-
Epidote	Epidote	Epidote	Epidote
Muscovite	Muscovite	Muscovite	Muscovite
Quartz	Quartz	Quartz	Quartz
Chlorite	Chlorite	Chlorite	Chlorite

\* Underlined type in Tables 1 and 2 indicates principal minerals; regular type -- minerals of secondary importance and minerals of rare occurrence at the localities.

Table 2

Sheregesh	Shalym	Tashtagol	Kochura
<u>Magnetite</u>	<u>Magnetite</u>	<u>Magnetite</u>	<u>Magnetite</u>
<u>Pyrite</u>	<u>Pyrite</u>	<u>Pyrite</u>	<u>Pyrite</u>
<u>Pyrrhotite</u>	Pyrrhotite	Hematite	Hematite
<u>Sphalerite</u>	Chalcopyrite	Chalcopyrite	Chalcopyrite
Marcasite	Chalcopyrite	Sphalerite	Sphalerite
Chalcopyrite	Hematite	Galena	Tetrahedrite
Galena	Arsenopyrite	Bornite	
Hematite	Galena	Tetrahedrite	
Bismuthinite	Molybdenite		
Molybdenite	Bismuthinite		
Bornite	Chalcocite		
Chalcocite	Bornite		
Cubanite			
Valleriite			
Arsenopyrite			
Altaite			
Linneite			

In the Shalym skarns pyroxene is considerably less abundant, scapolite and spinel are even less so, and olivine, wollastonite and idocrase are absent.

At the Tashtagol deposit, there is no pyroxene in the skarns, which

consist mainly of garnet. In the Kochura deposit there is practically no garnet.

On the other hand, in passing from Sheregesh to Kochura, the amount of medium- and low-temperature minerals — epidote, muscovite (sericite), quartz, chlorite, etc. — increases considerably, and the ore minerals include hydrothermal hematite.

In the same direction there is a decrease in the intensity of replacement of the aluminosilicate rocks by the skarn minerals and magnetite. The endoskarns are most widely developed in Sheregesh and slightly less in Shalyma. In these deposits, magnetite ores replace not only the carbonate rocks but also endoskarns and even unaltered (or slightly altered) syenites, gabbro porphyries and other rocks.

At Tashtagol and especially at Kochura, endoskarns are absent or are very scarce. Magnetite ores were formed here by selective replacement of carbonate-bearing rocks, sometimes with perfect preservation of bedding.

It is well known that not only the formation of minerals but also the amount of admixed elements in individual minerals is determined to a large extent by the physicochemical environment. Hence the characteristics of distribution of admixed elements in the ore minerals may serve as an additional criterion for judging of the conditions of ore deposition.

Bearing this in mind, the author undertook a detailed study of the chemical composition of the magnetites separated from different types of ore in each of the deposits of the region. The selection of magnetite for this kind of geochemical study was not arbitrary. Magnetite is the principal ore mineral in the deposits and its crystallochemical properties are such that it captures many elements which can be successfully used in geochemical investigations. Moreover, it is strongly ferromagnetic and can easily be separated from the ores and rocks in amounts needed for various analyses.

To obtain as nearly pure magnetite fractions as possible (monomineralic), use was made of the magnetic separator constructed by S. S. Lapin, Senior Scientific Associate of the Institute of Geology and Geophysics. The samples of magnetite ore (or magnetite fractions separated from rocks) were ground to a very fine powder in an agate mortar. The powders were passed through the magnetic separator activated by three-phase alternating current. The separation is accomplished in this instrument by a magnetic flux opposing a stream of water.

The chemical analyses of the magnetite fractions are given in Table 3. It should be noted that, in spite of the adopted procedure, it was impossible to obtain completely homogeneous material. This was revealed by the presence in the samples of small amounts of silica and lime, which are not likely to be present in magnetite as isomorphous admixtures. On the other hand, the main mass of the other oxides, especially  $\text{TiO}_2$  and  $\text{MnO}$ , is undoubtedly present in the crystal lattice of magnetite. This is proved by the absence of other Ti and Mn-bearing minerals (besides magnetite) not only in the analyzed material but also in the original crude samples of the ores. Variations in the content of these elements are, therefore, worthy of attention.

Some analyses show an excess of  $\text{Fe}_2\text{O}_3$  in magnetite, probably due to partial oxidation occurring during the preparation of samples (grinding and drying) and while the fine magnetite powders awaited analysis.

Manganese is present in all samples of magnetite. However, its maximum content characterizes the Sheregesh deposit, in which the average content of  $\text{MnO}$  is 1.09%. In the Shalym magnetites, the average  $\text{MnO}$  content decreases to 0.31%, and in the Tashtagol and Kochura magnetites, it is



Table 3  
Chemical Composition of Magnetites (% by wt.)

Specimen number	Sheregesh					Shalym					Tashtagol					Kochura					
	21	1188	1259	880	1003	Aver-age	320	633	1090	1098	Aver-age	1338	1409	1126	1	Aver-age	1041	568	1039	1044	Aver-age
SiO <sub>2</sub>	0.26	0.62	0.32	1.38	0.86	—	0.21	1.50	0.76	1.94	—	0.68	0.61	1.25	0.35	—	0.42	1.08	1.10	1.31	—
TiO <sub>2</sub>	0.32	0.20	0.76	0.20	0.32	0.36	0.29	0.13	0.10	0.19	0.18	0.10	0.25	0.23	0.07	0.16	0.25	none	0.23	0.15	0.16
Al <sub>2</sub> O <sub>3</sub>	2.48	1.51	0.87	3.11	2.33	2.06	1.92	0.70	1.75	1.50	1.47	2.09	0.73	0.77	0.72	1.08	1.54	0.90	0.22	1.92	1.14
Fe <sub>2</sub> O <sub>3</sub>	71.81	69.57	68.35	68.61	71.81	—	—	66.14	70.92	67.74	—	72.71	69.30	67.30	—	—	—	66.96	68.61	—	—
FeO	25.50	25.11	29.96	26.73	26.32	—	—	30.20	25.11	29.45	—	24.30	29.24	30.23	—	—	—	29.55	29.06	—	—
Fe (misc.)	69.99	—	—	—	70.31	—	72.19	—	—	—	—	—	—	—	72.09	—	71.56	—	—	70.94	—
MnO	1.60	2.06	0.39	0.90	0.50	1.09	0.30	0.13	0.33	0.46	0.31	0.04	0.25	0.05	0.11	0.11	0.02	0.19	0.05	0.02	0.07
MgO	1.79	0.83	0.18	0.69	0.18	0.53	0.18	0.36	0.98	0.29	0.45	1.03	0.23	0.04	none	0.33	0.47	0.47	0.04	0.33	0.32
CaO	none	none	0.10	0.80	none	—	none	0.31	none	none	—	none	0.35	0.45	0.03	—	none	0.10	1.05	none	—
Total	99.73	99.97	100.93	102.42	99.40	—	—	99.47	99.95	101.57	—	100.95	100.90	100.32	—	—	—	99.25	100.36	—	—

Note. Chemical analyses of specimens 1269, 633, 1098, 1409, 1126, 568 and 1039 were made at the laboratory of the Chemical-Metallurgical Institute ZSFAN SSSR (A. E. Korotikh, analyst); of specimens 21, 1188, 880, 1003, 320, 1090, 1338, 1041 and 1044, at the beneficiation laboratory of the Mining Institute ZSFAN SSSR (V. V. Krushevskaya and V. G. Volstikhina, analysts). Specimen 1 was analyzed at the Central Chemical Laboratory of ZSGU.

Note. Comma represents decimal point.

0.11 and 0.7%, respectively.

The data on the MnO content in the magnetites of the Kondoma group appear also in N. D. Sindeeva's work [4]. This author gives the following figures (% by weight) for the MnO content: in the Sheregesh magnetites, 0.68, 1.25, 1.44 and 1.78 (the average of 4 analyses = 1.3%); in the Tashtagol magnetites, 0.14, 0.15, 0.26 and 0.22 (0.19% on the average); and in the Kochura magnetites, 0.12 and 0.82. These figures, with the exception of one analysis of Kochura magnetite, are very near to the analyses given in the present paper, and they confirm the uniform decrease in the average MnO content in the magnetites in passing from the high temperature Sheregesh deposit to the low temperature Kochura deposit.

Titanium is the usual isomorphous admixture in magnetites. The highest titania content is found in the Sheregesh magnetites (0.36%); the lowest, in the Tashtagol and Kochura magnetites (0.16%). The magnetites of the Shalym deposit occupy an intermediate place. According to the chemical analyses, the average content of MgO and  $Al_2O_3$  in the magnetites changes in the same direction. The results of determinations of zinc in the magnetites are given in Table 4.

Table 4

Average Zinc Content  
in Magnetites (wt. %) \*

Locality	Total number of analyses	Zn
Sheregesh	15	0.049
Shalym	10	0.040
Tashtagol	11	0.023
Kochura	11	0.007
Mustag granites	4	0.055

\* Zinc was determined polarographically  
by I. L. Ruzinova

The method used in preparing magnetite samples eliminates mechanical admixtures in the form of sphalerite or some other zinc-bearing mineral. To confirm this, a second (control) determination of zinc was made on the same magnetite samples after they had been ground and passed through the magnetic separator twice more.

The figures for the zinc content in the control samples showed slight positive and negative deviations from the results of the first determination but did not exceed the limits of analytical error.

That the analyzed material was free from zinc-bearing minerals (sphalerite) is indicated also by the fact that the character of distribution of zinc in the magnetites does not depend on its average content in the ores. For example, the Kochura ores are, on the whole, richer in zinc as compared with the Tashtagol and Shalym ores, while the Kochura magnetites are least contaminated with zinc and other elements. In general, the regular variation in the average zinc content in the magnetites from different deposits was very clear.

For comparison, zinc was determined in the accessory magnetite from the granites of the Sarlyk-Mustag pluton. The average zinc content in this magnetite, according to four analyses, is 0.055%, i.e., higher than the maximum zinc content in the magnetites of the Sheregesh iron deposit.

The results of determinations of gallium are shown in Table 5. The analyses of magnetite samples for gallium were made in the analytical laboratory of the Chemical-Metallurgical Institute of the West Siberian Affiliate of the Academy of Sciences by M. S. Zolotareva. In spite of the small number of analyses, the distribution of gallium in magnetites showed the same regularities as zinc, titanium and other admixed elements.

The irregularity introduced by the gallium content in the Shalym magnetites may be ascribed to the small number of determinations on the Shalym samples and on the magnetites from the entire Kondoma group of deposits.

To clarify this point, a graph showing variations in the average content of admixed elements in the magnetites of the Kondoma region was constructed (see graph).

The general regularity in the distribution of Ti, Mn, Zn and Ga is evidently characteristic of some other admixed elements as well, and this was confirmed by spectrographic analyses for Cr, Sn and, in part, for Co.

Thus, the average content of admixed elements in the magnetite deposits varies regularly in passing from Sheregesh to Kochura, i. e. in the same direction in which high temperature mineral assemblages are replaced by the lower temperature assemblages.

The regular variations in the content of the admixed elements in magnetites indicate, on the one hand, that the physicochemical conditions of ore deposition were different in these deposits, and, on the other, emphasize the genetic unity of the Kondoma group of iron deposits.

It was noticed by geologists long ago that the contact metasomatic deposits in Western Siberia occur in groups. If the regularities in the distribution of admixed elements in the magnetites of the Kondoma region discovered by the author are confirmed by investigation in other regions, then the knowledge of the composition of the magnetites should make it possible to determine the position of a given deposit in a series of deposits belonging to a single genetic group. This information may have certain practical value as an additional geochemical criterion in directing exploratory work and in determining the maximum beneficiation of the magnetite ores obtainable by the usual methods so far as admixtures detrimental to the metallurgical processes (for example zinc) are concerned.

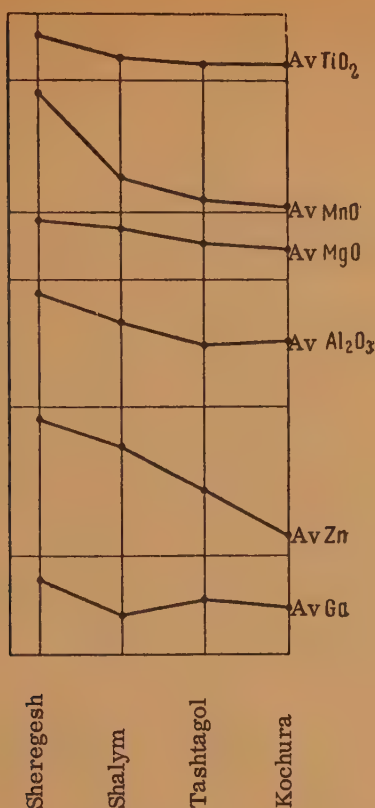
In conclusion, it should be noted that according to the available data, the content of admixed elements in magnetite and in a number of other minerals of a given deposit is not the same for all samples. However, these data are still insufficient to provide full information on the regularities of distribution of admixed elements in individual deposits or ore bodies. This is a problem for further investigation.

The zonal distribution of the sulfides presented a somewhat more difficult problem (Table 2). The ores of Sheregesh and, after it, of Shalyma,

Table 5

Average Gallium Content  
in magnetites (wt. %)

Locality	Total number of analyses	Ga
Sheregesh	7	0.00142
Shalym	9	0.00074
Tashtagol	7	0.00100
Kochura	4	0.00087



Average content of admixed elements in magnetites. One millimeter on the vertical axis equals 0.55% for  $\text{TiO}_2$ , 0.05% for  $\text{MnO}$ , 0.05% for  $\text{MgO}$ , 0.10% for  $\text{Al}_2\text{O}_3$ , 0.002% for  $\text{Zn}$  and 0.0001% for  $\text{Ga}$  (percents by weight).

are the richest in quantity and variety of sulfides. The ores of Tashtagol contain negligible amounts of sulfides and particularly of pyrite.

This caused some investigators to conclude that there is in the region a "zoning of ore minerals which is the reverse of normal" [1]. However, in the terminal Kochura deposit, the content of sulfides increases sharply. If the ores of the Turgenevsk polymetallic deposit are included, the zonal arrangement of the ores as depicted by Batov [1] and some later investigators is completely destroyed.

In the author's opinion, this is quite natural so far as sulfide and polymetallic mineralization are concerned, for the region was mineralized not once but twice [2]. The later mineralization, genetically related to the granitic pluton, produced independent ore deposits and was also, to a



greater or less extent, superimposed on the iron mineralization, masking and complicating the zoning of the ores produced by contact metasomatism.

## REFERENCES

1. Batov, N.A. (1935) Geologiya i Mineralogiya Zhelezorudnykh Mestorozhdenii Kondomskoi Gruppy (Geology and mineralogy of the iron deposits of the Kondoma region). Mater. po Geologii Zap. Sib. kraya, vyp. 18, Tomsk.
2. Vakhrushev, V.A. (1958) O Geneticheskikh Svyazyakh Zheleznogo i Polimetallicheskogo Orudneniya s Intruziyami v Kondomskom Raione Gornoi Shorii (On the genetical relation between iron and polymetallic mineralization and the intrusives in Gornaya Shoriya). Zap. Vses. mineralog. o-va, ch. 87, vyp. 2, p. 151.
3. Derbikov, I.V. (1957) O Zonal'nosti Litofil'nykh Elementov Skarnovykh Mestorozhdenii Zheleza Zapadnoi Sibiri (Zonal distribution of lithophile elements in the skarn iron deposits of Western Siberia). Sb. Tezisy dokladov XI otchetn. nauchn. sessii Zap. Sib. filiala AN SSSR, Novosibirsk.
4. Sindeeva, N.D. (1934) Vynos Margantsa iz Zhelezorudnogo Kompleksa. Sb. Materialy po Petrografii i Geokhimii Kuznetskogo Alatau i Altaya (Removal of manganese from iron ore complex. In the collection: Petrography and geochemistry of Kuznetskii Alatau and Altai), pt. I, Izd. Akad. Nauk SSSR.

Received for publication  
October 24, 1958.



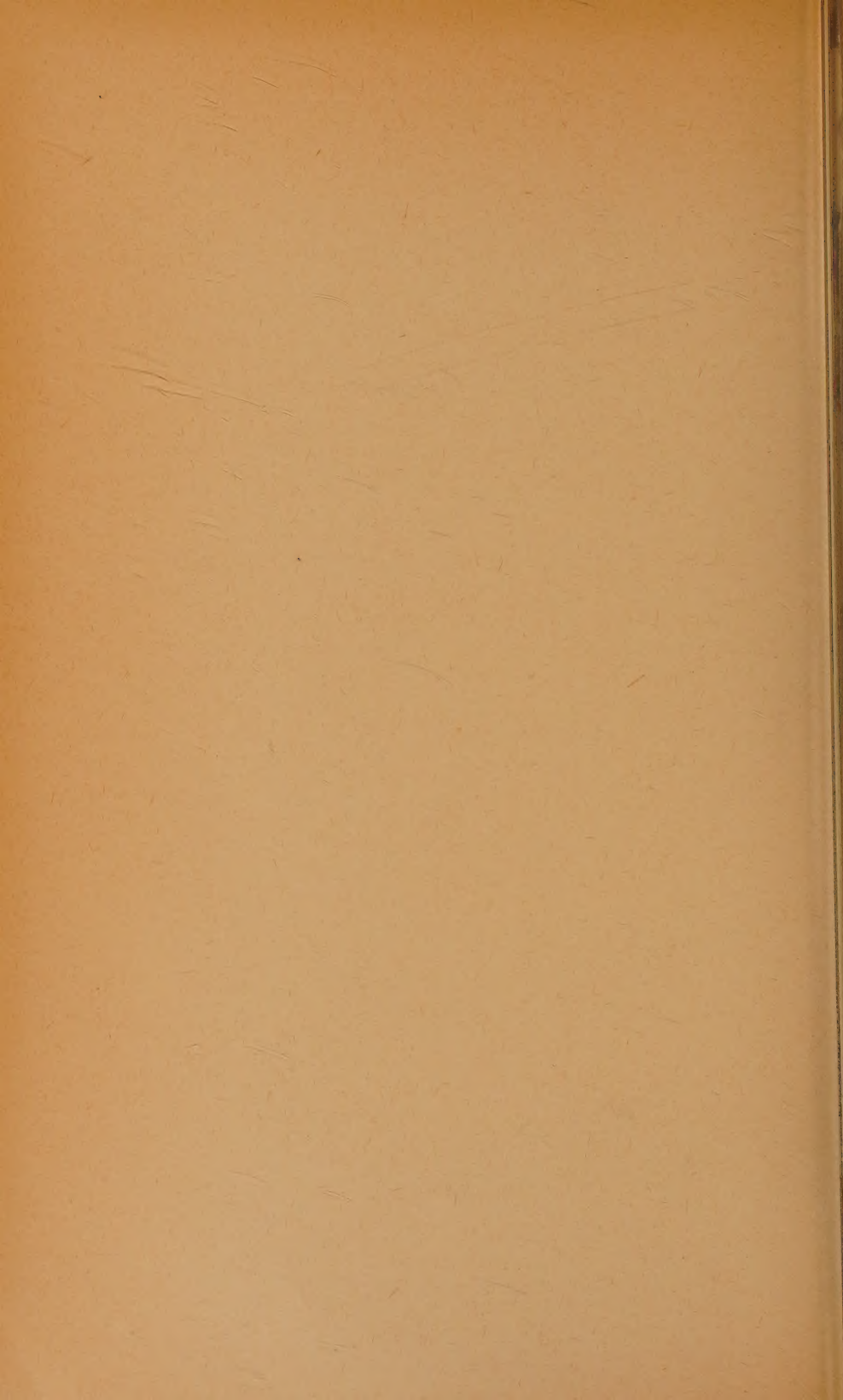












Geokhimiya began publication in 1956 under the able editorship of A. P. Vinogradov. It is the Soviet counterpart of Geochimica et Cosmochimica Acta, having practically identical fields of interest and coverage and publishing approximately the same number of pages per year. With the great increase in geochemical research in the U. S. S. R., there have come into being a number of highly specialized journals in geochemistry and related fields. It is probably better to begin translating this more general journal first and follow with some of the more specialized ones if interest appears to justify this course of action and if the financial arrangements can be made.

An initial grant from the National Science Foundation in 1958 enabled the Geochemical Society to translate and publish the eight issues for that calendar year. These issues have been very well received by a growing list of subscribers in most of the countries of the Western world.

Many inquiries have been received concerning back issues (1956 and 1957) and continuation of the program for issues after 1958. The National Science Foundation has made additional grants for translation and publication of the issues for 1956, 1957 and 1959. These are being translated and issued as rapidly as they can be processed. Prices are the same as for the 1958 issues (see inside front cover). Subscriptions and orders for single copies should be sent to the Geochemical Society in care of the undersigned.

The National Science Foundation has continued to be most cooperative in this venture. They are continuing support of the project although subscriptions are too few to make it anything like self supporting thus far. It is hoped that subscribers will call attention of other interested workers to the availability of the translation of Geokhimiya so that these important research papers can be made more generally available to those interested in geochemical and related investigations.

Earl Ingerson  
Translation Editor  
Department of Geology  
The University of Texas  
Austin 12, Texas

---

In matters of subscription for Geokhimiya refer to: Moskva K-104, Pushkinskaya, 23, Akademkniga. Chief Editor: A. P. Vinogradov. Editorial Council: V. I. Baranov, K. A. Vlasov, V. I. Gerasimovskii, D. S. Korzhinskii, A. A. Saukov, N. I. Khitarov (Responsible Secretary), V. V. Shcherbina (Deputy Chief Editor).



Geochemical News is an informal bi-monthly newsletter published by the Geochemical Society and sent without charge to all of its members. It contains news of the activities of the Society, such as summaries of Council Meetings, reports of committees and plans for the future. It also includes announcements of forthcoming meetings and symposia of interest to geochemists, personalia, announcements or short reviews of books of geochemical interest, information on translations and translation services, letters and short notes by members, etc.

Subscriptions are available to institutions at \$2.00 per year. Orders should be sent to the Treasurer:

Dr. George T. Faust  
U. S. Geological Survey  
Washington 25, D. C.

Individuals who wish to receive the News should join the Geochemical Society. Application blanks are available on request from the Secretary, Dr. Konrad B. Krauskopf, Stanford University, California. Dues are \$2.00 per year.

---

Geochimica et Cosmochimica Acta is the official journal of the Geochemical Society. It is an international journal interested in the broad aspects of geochemistry, both geographically and subject-wise; articles have been received from contributors from all of the (inhabited) continents.

New chemical data and interpretations involving chemical principles are emphasized. For example, papers in chemical mineralogy, petrology, oceanography and volcanology are acceptable, as are those in the chemistry of meteorites, whereas it would be suggested that those in descriptive mineralogy and volcanology, petrography, physical and biological oceanography and physical meteoritics, be sent to other journals specializing in these subjects.

Thus, the subject coverage is closely similar to that of Geokhimiya. Also, the number of pages published per year is of the same order of magnitude. Subscription prices are as follows:

To members of the Geochemical Society-----	\$10.00 per year
To other individual subscribers -----	\$20.00 per year
To libraries, laboratories, and other institutional subscribers -----	\$46.50 per year

Orders for subscriptions should be sent to: Pergamon Press, 122 E. 55th Street, New York 22, New York or Headington Hill Hall, Oxford, England.